

# METALLURGIA

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## Strategic Minerals in the United States

*Considerable attention is being given to strategic minerals in the United States, and deposits are being explored in that country which are either partly developed or in which ore is in sight, and from which further exploration may reveal additional ore. The position with regard to antimony, chromite, manganese, mercury, nickel, tin and tungsten is briefly reviewed.*

**I**N an emergency, such as the sudden stoppage of overseas supplies, the United States may be able to turn to domestic deposits for mercury and antimony, but for tin and some other strategic materials, it may have to depend almost entirely upon accumulated stocks and substitutes. In his report to the Secretary of the Interior, Dr. E. R. Sayers, Director of the Bureau of Mines, stated that although mining engineers of the Bureau have examined United States deposits of various metals listed as strategic by the Army and Navy Munitions Board, much of the ore so far encountered is low grade or of such a quality that will require considerable metallurgical research to make it usable.

Up to March of this year exploratory operations had been conducted by the Bureau on 32 deposits in 12 States; seven of these projects have been completed, three were held up because of weather conditions, and 22 are still active. In addition, plans had been made for starting work in six other areas as soon as weather conditions permitted. Of the deposits upon which work has been done or is in progress, two deal with antimony ore, three with chromium ore, fifteen with ores of manganese, three with mercury ore, two with nickel ore, two with tin, and five with tungsten.

In considering deposits for exploration, Dr. Sayers states that the Bureau is interested in three general types or groups of deposits which are not necessarily differentiated geographically. These are the partly developed deposits or deposits with some ore in sight or from which ore has been shipped, further exploration of which promises to reveal additional ore; extensive low-grade deposits, the continuity of which in depth and along the strike and the average grade of which are unknown because they have not warranted exploration and development by private industry. Although sub-commercial under normal conditions, such deposits merit special consideration for strategic purposes as they may be capable of furnishing important tonnages of metal should there arise such conditions that cost becomes secondary. In addition, deposits are included which are relatively small individually, but are representative of a type occurring in sufficient number within a region or extensive geological formation to contain in the aggregate considerable reserves.

The results of the Bureau's investigations are as follows:

### Antimony

Two antimony projects have been undertaken to date, one in Valley County, Idaho, the other in Kern County, Calif. Definitely encouraging results have been obtained from the work on two separate deposits in the Yellow Pine District of Idaho, on one of which the presence of high-grade antimony ore was disclosed; this is of unknown

extent but probably is not large. Shipments of ore from this area were begun last October.

Concentrates of the Yellow Pine District ore contained arsenopyrite, stibnite, gold and silver. The problem was to produce an acceptable grade of metallic antimony and recover the previous metals from these concentrates. The general schemes decided upon was to produce a crude antimony bullion containing the precious metals and to refine this electrolytically to give antimony at the cathode and collect gold and silver in the slimes.

The other deposit is a large low-grade mineralized mass of granite, the extent and average grade of which is being delineated by diamond drilling. Although the limits of this deposit have as yet not been determined, enough has already been learned of its extent and grade to warrant the belief that it comprises an important strategic reserve of antimony.

### Chromite

Of three projects for the development of chromite deposits, undertaken in Grant County, Oreg., Natrona County, Wyo., and Stillwater County, Mont., one was definitely discouraging and two have been determined to be of sufficient importance to constitute valuable reserves.

One of the projects has served to indicate the presence of a large tonnage of ore which, though sub-commercial under known technology, could be utilized in time of stress to provide an important tonnage of chromite for national defence purposes. Work on this project has served to develop the deposits to a stage where definite plans are being made to insure their development and active production of ore. Another of the projects has revealed smaller tonnages, but the ore is close to the surface and can be developed quickly so that production can start in a short time. These ores, being high in iron, are suitable for chemical purposes, but their use as a source of high-grade ferrochrome for the manufacture of alloys would involve costly beneficiation.

As an integral part of the strategic minerals programme the Metallurgical Division of the Bureau of Mines is making investigations on the utilisation of the high iron chromite. To expedite the solution of the problem several methods of attack were followed, including electrolysis in aqueous baths, electrolysis in fused baths, matte smelting and electrothermal milling. Promising early results have been obtained, and it is hoped that with the completion of additional facilities, now under construction, methods will be developed for the utilisation of these ores in established commercial plants.

### Manganese

Work on manganese deposits was not started until late in 1939, and none of the projects has been completed. In

only one instance have these projects been definitely discouraging, and even in this instance a small deposit of metallurgical ore of direct shipping or high-grade was disclosed and extensions of other lower-grade deposits have been found. In one area, important tonnages of a fair grade of ore not hitherto known to exist are being disclosed adjacent to previously known deposits which furnished some manganese during the last war. At another project, recently started, diamond drilling has already indicated a continuity of the ore that could not be assumed previously, and is furnishing information that will permit of estimating ore reserves with much greater confidence than was previously possible. At another project which has furnished some metallurgical ore, diamond drilling operations are indicating greater tonnage than was previously known to exist. In still other instances, extensions of known deposits of manganiferous ore are being found.

Most of the manganiferous deposits being developed are of such a nature that a metallurgical problem is involved in their utilization. While some ores, for example, may be near metallurgical grade except for too much silica and can be treated by simple flotation process, and others may have too low a manganese-iron ratio but have possibilities of being treated by magnetic separation, still others are of such a grade that known ore-dressing methods are ineffective. For example, some such ores contain high-iron, high-silicate and high-lime contents which are intimately associated, and these ores may also contain such deleterious elements as zinc, copper and lead which render them unfit for metallurgical use. The Bureau of Mines has recently started on a programme to develop methods for treating domestic low-grade manganese ores. Experiments carried out in the laboratory have given encouraging results, and these methods will be tested out on a larger scale in pilot plants now being constructed and which are expected to be placed in operation some time this summer.

Methods which America's steel industry might employ to save considerable quantities of manganese are suggested by Dr. Sayers:—

- (1) Economy in the use of manganese by making certain that the steel does not contain more manganese than is necessary.
- (2) Substitution of alloys containing less manganese for those containing more, for example, the substitution spiegeleisen for ferro-manganese. Ores suitable for the former product are relatively more abundant in the United States.
- (3) Substitution of other deoxidising agents such as zirconium and titanium.
- (4) Substitution of other agents for modifying properties, such as nickel and chromium.
- (5) Use of furnace procedures designed to yield a high residual manganese metal at the end of the heat and thus make possible smaller additions of manganese alloy.

A study made by the Bureau of Mines several years ago proposed the use of a silicon-containing spiegeleisen having 20% manganese, and also of a special alloy containing 30% manganese, both of which can be manufactured from ores available in this country. An estimate of the potential tonnage of alloys of this type shows that enough can be obtained from ores in the Cuyuna district (of Minnesota) alone to supply the steel industry for a considerable period.

### Mercury

Of three projects for the exploration of mercury deposits, one project in Humboldt County, Nev., has been completed. Through the development of a technique for exploring the favourable areas in this district, one small deposit (the depth of which has not been ascertained) of commercial grade mercury ore was discovered. Production has already been started upon this deposit. Of the two

other mercury projects, one near Coeo Springs, Calif., and the other in Pike County, Ark., work is progressing by means of diamond drilling as well as surface exploration.

### Nickel

Two projects, one in Stillwater County, Mont., and the other in Clark County, Nev., have been selected as the least unfavourable. Work has progressed far enough to indicate that appreciable tonnages of commercial material are not likely to be found. Work will be continued for some time on one deposit which, although low-grade, probably contains a large tonnage.

### Tin

Work on two tin-bearing areas, in the Black Hills section of South Dakota and Catron and Sierra Counties, N. Mex., has served to confirm the conviction that the maximum output of tin possible from domestic deposits would be an inconsequential factor in supplying the essential requirements of defence and related industry. In one of these deposits, however, extensions of previously known very low-grade deposits were found.

### Tungsten

Projects on tungsten undertaken in Mono County, Calif., and Pershing County, Nev., have revealed erratic deposits of low-grade ore. Some extensions of the known ore limits were developed, but the ore is sub-commercial and the deposits cannot be considered to constitute a substantial reserve. The Bureau has recently started work in Inyo County, Calif., in White Pine County, Nev., and in another section of Pershing County, Nev., but has not progressed sufficiently to arrive at conclusions, although in each case some ore in addition to that previously known to exist has been disclosed.

A high grade deposit of tungsten ore has been discovered in the Yellow Pine District, Valley County, a district well known for its antimonial gold ores, but not previously known to contain tungsten. Although assay returns had not been completed and diamond drilling was still being continued, scheelite ore of commercial grade has been encountered by four drill holes spaced over a length of more than 300 ft. with indicated widths of 5 to 25 ft. Several 5 ft. sections have assayed over 5% tungsten trioxide ( $WO_3$ ). Ore deposits containing as little as 0.75% if fairly extensive, are generally considered as being commercial grade. This deposit, if it proves to be large, will therefore be of great importance.

Analytical procedures for the various ores of antimony, chromium, manganese, nickel, tin and tungsten are given by the Bureau in enough detail, with references, to enable any competent chemist to follow them. Certain parts that have been changed or developed in Bureau laboratories to assure accurate results and simplify the work are emphasised. For example, a cheap and efficient muffle for sodium peroxide fusions, that can be assembled in a few minutes is described in detail, and the following needed precautions to obtain uniform accurate tungsten analysis are enumerated: Grind the ore to pass 100 mesh, use a large amount of concentrated HCl, and heat to 60° C. for at least one hour. This appears to be necessary to dissolve the minerals of tungsten. Best results have been obtained by using cinchonine as a precipitating agent. The precision under the procedure outlined has been found to be accurate to as low as 0.05%.

In general, the Metallurgical Division of the Bureau of Mines conducts investigations relating to the treatment of ores and metallurgical products from the condition in which they are mined to the refined metal, with the object of conserving natural resources and eliminating waste by furnishing information on current methods of metallurgical practice, making fundamental studies of metallurgical processes, and developing new processes and alloys to the point of demonstrating their practicability or value.

# The Effect of Silver on Some Properties and on the Performance of Antimonial Lead Storage Batteries

**A**N investigation on the effect of from 0.05 to 0.15% of silver upon the properties and performance, in storage batteries, of lead alloys containing from 4 to 12% of antimony has been carried out by Fink and Dornblatt.\* No previous study of the effect of silver present in battery grid metal has been published, although some interesting properties of lead anodes containing silver have been known for some time. That the modern storage battery, so extensively used for starting, lighting and ignition purposes, has well-known but uncorrected deficiencies is evident from the annual report of the United States Secretary of Commerce, 1938, in which it is stated that experiments on various lead alloys as substitutes for the customary lead-antimony alloys have been continued. Cells containing no antimony are comparatively free from local action and show greatly reduced evolution of hydrogen, but have the disadvantages of corrosion of the positive grids and higher charging potentials. The lead alloy remains one of the most important subjects in battery research.

It is generally recognised that definite advantages are obtained in the use of antimonial lead over pure lead plates, but it is also appreciated that these alloy plates have many deficiencies in service. The possibility of overcoming some of these deficiencies, without sacrificing the beneficial effects of antimony, by adding silver to the grid metal was suggested by the knowledge that lead containing silver has superior resistance to corrosion, as is indicated by the data on the use of lead-silver alloys as insoluble anodes. The addition of silver to lead-antimony grids would be justified commercially if, as a consequence, the shortcomings of the lead-antimony grid alloys were overcome wholly or in substantial part, or the antimony content could be materially reduced, so that the additional cost due to silver would not be excessive and offset by any advantages gained.

TABLE I.  
ANALYSIS OF ANTIMONIAL-LEAD GRID ALLOYS USED IN BATTERY TEST.

Sb. %	Ag. %	As. %	Su. %	Cu. %	Bi. %	S. %	Fe. %
11.88	0.0015 0.052 0.10 0.149	0.03	0.18	0.016	0.021	0.0026	0.0003
11.76		0.03	0.18	0.020	0.025	0.0026	0.0003
7.92	0.003 0.051 0.106 0.149	0.03	0.19	0.034	0.020	0.0026	0.0003
7.86		0.02	0.19	0.033	0.018	0.0026	0.0003
5.94	0.0028 0.049 0.106 0.152	0.02	0.20	0.010	0.020	0.0028	0.0003
6.00		0.02	0.19	0.014	0.020	0.0026	0.0003
4.14	0.004 0.052 0.103 0.152	0.01	0.22	0.033	0.018	0.0010	0.0003
4.02		0.01	0.18	0.025	0.015	0.0019	0.0003

In view of the highly competitive nature of the storage battery industry, it was considered advisable to keep the silver concentrations of the experimental alloys low enough to open a wide market in the event of such small additions proving beneficial. On this basis, the upper limit for the silver content of the alloys used in this investigation was arbitrarily set at 0.15%. The increase in cost due to this silver content is not large in proportion to the cost of the assembled battery, and would be justified by even a moderate improvement in performance. With

regard to the antimony content, the authors state that this metal is a strategic one and, at the present time, there are good reasons for desiring to use less of it in so vital a commodity as the storage battery. The investigation was made on a series of alloys containing silver, the compositions of which are given in Table I., and the effects of this addition on the physical properties, anodic resistance and on battery performance, were determined. A study was also made of the variation in electrode potential as a function of time, composition and current density.

Under the conditions of this investigation the effect of the addition of 0.05-0.15% silver upon the properties of 4.0 to 12% antimonial-lead alloys and their performance as storage battery grids may be summarised as follows:—

1. The anodic corrosion of the antimonial-lead alloys is very substantially reduced. For practically complete inhibition of general and pitting corrosion of these alloys, 0.05% silver is inadequate, but from 0.10 to 0.15% silver is extremely effective.
2. The amount of antimony dissolved from the anode and deposited on the cathode is greatly reduced by adding 0.15% silver to the anode. This effect probably occurs to substantially the same extent with 0.10% silver, and to a lesser extent with 0.05% silver.
3. Silver, when present in the antimonial-lead to the extent of 0.05 to 0.15%, is not appreciably dissolved out of the anode, and does not deposit upon the cathode.
4. Anodic polarisation is decreased by the presence of silver in the alloy. This effect is small with not over 0.15% silver but increases with increase of silver content of the alloy, and may be quite significant in alloys containing about 1% or more silver.
5. Chill-cast antimonial-lead grid alloys containing 4 to 8% antimony can be heat-treated with marked improvement in strength and some improvement in conductivity; the addition of 0.05-0.10% silver increases the maximum strength obtainable by about 20%. The highest strength is obtainable in the alloys containing 4% antimony. In the absence of heat-treatment, up to 0.15% silver has no significant effect on the strength of these alloys.
6. The author's data for grid alloys containing 4 to 12% antimony and 0.00 to 0.15% silver show that the life of the batteries was, on the whole, prolonged about 4% when 0.05-0.15% silver was present in the grid metal. It has, therefore, been demonstrated that as much as 0.15% silver can be present in antimonial-lead grids without any adverse effect on battery life, and that from 0.05-0.15% silver probably is beneficial in this respect.
7. It has been shown that the presence of 0.05-0.15% silver in the anode grid definitely will not cause the battery to suffer a serious loss of charge; actually there is some indication that about 0.10% silver in the antimonial-lead anode reduces the loss of charge of the negative plates.
8. Batteries whose grids contain silver are less likely to overheat on overcharge.
9. Some of the deficiencies of the present antimonial-lead storage battery may be overcome by (a) adding 0.10% silver to the present grid alloy used for the positive plate, or (b) adding 0.10% silver to both

\* Colin G. Fink and Albert J. Dornblatt, The Electrochemical Society General Meeting, April, 1941. Preprint 79-10.



positive and negative plates of the 4% or the 6% antimony alloys and using the grids in the heat-treated condition.

The results of this investigation indicate that storage batteries with heat-treated 4% antimony—0.10% silver alloy grids will excel the conventional storage battery in one or more of the following characteristics: Corrosion-resistance of positive plates, ruggedness, battery life, retention of charge, low temperature rise on overcharge. The performance of the conventional battery will probably be similarly improved, except as regards strength of the grid metal, by merely adding 0.10% silver to the grid alloy. To do this increases the cost but slightly. In the

case of the heat-treated alloy, the cost is not increased, and may even be slightly reduced as a consequence of replacing from 4 to 8% antimony by 0.10% silver.

The authors feel that the results of this investigation are indicative, if not conclusive, with respect to worthwhile improvement in lead storage batteries. Studies embracing a large number of batteries, and of a commercial nature, appear warranted. Should such studies confirm the indications reported here, the general adoption of low-antimony low-silver grid alloys might ensue, and in this event progress would have been made in solving a problem of national importance, relating to the strategic importance of antimony.

## The Rolling of Magnesium Alloy

**F**URTHER work has been carried out by Professor W. R. D. Jones and L. Powell.\* This investigation was carried out on lines similar to those recorded in a previous report,<sup>1</sup> summarised in our October, 1940, issue, and deals with experiments made to study the effect of cold work and subsequent annealing on an alloy of magnesium chosen on account of its proved general usefulness. The work described consisted of the production of 10-gauge sheets which were then cold rolled with varying degrees of deformation to 16-gauge. The sheets were subsequently annealed at different temperatures and tested. The experiments were carried out in two stages: (1) on sheets rolled direct from cast slabs, and (2) on sheets rolled from slabs extruded from a chill-cast circular ingot that had been teemed from the same ladle of molten alloy. In this way a comparison would be made between the properties of sheets rolled from cast slabs and those rolled from an extruded slab of the same composition. If the initial extrusion operation now generally carried out on the ingot could be eliminated, the production of magnesium alloy sheets might be cheapened.

The analysis of the material in the ladle from which the slabs were cast was: Manganese 2.28%, aluminium 0.05%, silicon 0.02%, copper 0.01%, and zinc a trace. The slabs were cast by Messrs. Magnesium Elektron Limited, using the mould described in the previous report.<sup>1</sup> The surfaces of the ingot slabs were sufficiently good not to require machining before the slabs were rolled.

TABLE I  
ROLLING OF THE SHEETS FROM 10 TO 16 GAUGE.

Original Length of Sheet at 10 Gauge, in.	Amount of Extension by Hot Rolling, in.	Thickness after Hot Rolling (Approx.), in.	Amount of Extension by Cold Rolling, in.	Final Length at 16 Gauge, in.	Cold Extension,* Per Cent.
30	30.0	0.064	nil	60	nil
30	28.5	0.064	1.5	60	5
30	27.0	0.067	3.0	60	10
30	22.5	0.080	7.5	60	25
30	15.0	0.087	15.0	60	50
30	7.5	0.097	22.5	60	75
30	nil	0.123-0.128	30	60	100

\* 10% cold extension means that the 16-gauge sheet was produced from the 10-gauge sheet by a combination of hot and cold rolling such that the sheet received 10% cold rolling, which followed 90% hot rolling—the 10-gauge sheet 30 in. long was extended by hot rolling by 27 in. to give a hot-rolled sheet 57 in. long; this was annealed at 450° C. for 1½ hours and then extended by cold rolling a further 3 in. to give a sheet 60 in. long ( $\frac{3}{57} = 10\%$ ,  $\frac{30}{57} = 90\%$ ).

The rolling operations were carried out on a Robertson 3-high, 24-in., non-reversing mill, using the rolling speed of 60 ft./minute. The rolls, in a highly polished condition, were pre-heated to about 90° C. for hot rolling. The slabs were heated at 450° C. for two hours and then hot rolled in the "straight" direction, i.e., that in which the metal had been teemed. The original thickness of the slab was  $\frac{11}{16}$  in., and the hot rolling was effected in four stages to bring the sheet to 10-gauge. The hot rolled 10-gauge sheets were annealed for 1½ hours at 450° C. and cooled slowly in the furnace. It was not necessary to pickle the sheets after heat-treatment.

The 10-gauge sheets (0.128 in. thick) were rolled down

to 16-gauge sheets (0.064 in. thick) by hot rolling, by cold rolling, or by a combination of these carried out in such a manner that the finished sheets, all at 16-gauge, had received the following percentage amounts of cold extension: 0, 5, 10, 25, 50, 75 and 100. A reduction from 10-gauge to 16-gauge means an extension of 100%. The length of a sheet sufficiently long to provide the test pieces required was 60 in., so that the length of the sheet at 10-gauge had to be 30 in. The rolling programme is given in Table I.

Sheets that were cold rolled from 10- to 16-gauge were very poor, and showed excessive edge cracking even with the small drafts that were used. In this case it was necessary to use intermediate annealing at 450° C. for half an hour until the thickness had been reduced to about 0.09 in., i.e., 13-gauge. The annealings were carried out when the sheets had reached the following gauges respectively, 11, 12 and 13. After the sheet had been reduced to 13-gauge the cold rolling to 16-gauge was performed without intermediate annealing. Intermediate annealing was not necessary for sheets that were given 75% or less cold work. Batches of sheets, each of which contained one sheet with each of these amounts of cold extension, were made up. One of these batches was tested in the unannealed condition, while the others were annealed for one hour at temperatures of 100°, 200°, 300°, 400° and 500° C. respectively.

Inside tests were carried out on an Olsen hand-operated 10,000 lb. machine using spherical-seated self-centring grips. B.S.I. test pieces were prepared from blanks sawn from the sheets at positions transverse, parallel and inclined at 45° to the direction of rolling.

The results of the tests are given graphically.

The general conclusions drawn by the authors from the series of experiments are as follows:

1. Sheets can be produced by rolling direct from cast slabs, which have mechanical properties at least equal if not superior to those produced from extruded slabs.
2. While small amounts of cold rolling slightly increased the tenacity, there was a more than corresponding decrease of ductility. Heavier cold work up to 75% extension does not further effect the tenacity appreciably. The thickness of the sheet before rolling was an important factor for higher amounts of cold extension.
3. Very small amounts of cold work are harmful and the inferior mechanical properties produced are not improved by annealing.
4. The mechanical properties of cold rolled sheets are not improved to any important extent by annealing. If annealing is carried out the temperature should not be higher than 300° C.
5. Rolling produces marked directional properties which are not eradicated by annealing at temperatures even up to 500° C.
6. There is no critical combination of cold work and annealing temperature that gives rise to excessive grain growth accompanied by decreased mechanical properties such as is known to be the case with certain other materials.

\* Jour. Inst. Metals, 1941, 37, 153.

<sup>1</sup> W. R. D. Jones and L. Powell, J. Inst. Metals, 1940, 30, 331.



# METALLURGIA

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## Use Your Energy in Britain's Cause

**W**E are to-day, as a nation, engaged in a conflict, on the outcome of which the future of mankind depends—whether the peoples of the world are to march forward along the broad highway of civilisation, with all their energies directed to the building up of an ever improving standard of social relationships, national and international, or whether they are to sink back into the slime of greed, tyranny and oppression in which men wallowed in the Dark Ages. It is true, of course, that, in the widest sense, the necessity for struggle or contest is still recognised as a fundamental fact, but with advancing civilisation it has been applied to industrial competition rather than to the militant spirit which now prevails, war being the earliest, the most primitive and the most brutal form of the struggle for existence.

The development of the social structure of the civilised world is due, in a large measure, to the steady and irresistible advance in that which sets the framework of our individual and social existence—the intimate knowledge of the world in which we live and its capabilities, all of which is summed up in the word "Science." It is continually contributing to the various branches of commerce and industry necessary to the maintenance and preservation of life and on improvements to increase the material resources of the world for the benefit of mankind. The measure of success achieved is, to a large extent, the measure of progress and of advancement of civilisation.

To-day, however, these advances are prostituted to the perpetuation, on a scale unparalleled in the past, of the militant spirit, and to Germany must be allotted the bad pre-eminence of the almost complete prostitution of science and industry to this spirit, the main characteristic of which is that its units are coerced into their various combined actions; there is no individual liberty, scarcely any possibility for the development of the individual life and there is compulsory co-operation.

In Britain we are under scarcely less a burden due primarily to our desire to preserve the degree of civilisation so patiently built up. We have concentrated our energies to the development of the social structure by industry which does not prosper by militancy. An industrial community, instead of stealing the means of life from its neighbours, or being enslaved by them—the enslaved people then performing the necessary industrial work—devotes itself as a whole to industrial activities. The need for co-operation may still be necessary, but it is voluntary rather than compulsory. The rise of industrial Germany was extremely rapid, but did not involve a disappearance of militancy, and Germany very well shows, not only in its military but also in its industrial aspects, those features of compulsory co-operation and regulation which are especially characteristic of militancy.

It must be appreciated that at the commencement of the present struggle Germany had been preparing for war for at least seven years, during which time her slogan had been "guns instead of butter," while our energies, during that time, were mainly concentrated on peaceful industrial pursuits. But, though unprepared for such a struggle, we took up the challenge for something that is fundamental, that is beyond human valuation: to defend moral values—liberty, good faith between men and nations, justice to strong and weak alike, the pledged word, and the common

decencies of what we have grown to regard as essential in civilised countries. This country had no alternative but to accept the challenge, and as a result many problems have had to be faced and many changes in our industrial and economic structure. It has, for instance, been necessary to adopt some of the characteristics of militant nations to interfere with individual liberty and institute compulsory co-operation, but there can be no doubt regarding the result of this struggle, providing every man and woman gives all that they have in brain and muscle unsparingly and unfalteringly to the common cause.

This war, in which we are engaged, is not only of troops and ships and aircraft, it is of whole populations, and the men and women of offices and workshops have the same responsibilities and share the same risks as those in the various armed Forces. It is for each individual member of the nation to accept his or her responsibilities and discharge them in the most competent and useful way. It is not enough to criticise the Government or any other official body for failures, whether apparent or real; self criticism on one's personal contribution to the war effort is just as vital. The ability to criticise the Government is a token of the individual freedom still enjoyed in this country, and by satisfactorily overcoming deficiencies displayed by self-criticism responsibilities will be undertaken which will assist in maintaining that freedom for ourselves and in freeing those who are now slaves of the common enemy.

The increasing intensity of the struggle has necessitated the greater concentration of industry to meet the essential requirements of the various Forces and to protect civilisation. The need for arms, ships and food is growing and must be satisfied. Many of those commodities, which we, as individuals, had grown to regard as essential requirements, will cease to become available to us until such times as sanity and good faith again prevails in the nations of the world. The sacrifice will be relatively small but it should be accepted with good will. Of greater hardship is that of individual trades and firms which have submitted with commendable cheerfulness and courage to the inevitable restrictions and controls which total war perforce imposes. The latest requirements for the concentration of industry are the logical corollary of the policy of limitation of supplies, since concentration in a limited number of factories will cheapen production, release labour and provide factory or storage space. But the process will be a painful one, and firms are justified in expecting an assurance that their position will be safeguarded when normal conditions are again restored.

There can be no doubt that industry generally is making great sacrifices, and making them willingly, for the common weal, and in return industry is entitled to ask from those concerned that every effort should be made to secure from the factories of the country the absolute maximum of production. Nothing should retard the war effort. Lack of essential supplies to our Forces may and does mean the loss of valuable lives, and it is in this direction that the individual responsibilities of those in munition or ordinance factories should be appreciated, whatever the position of the individual. The common cause demands nothing but the best from everyone. Let us, therefore, undertake our task and accept the personal inconveniences and difficulties arising from the policy of concentration and co-operation, in a real effort to save the world from destruction and to ensure that future generations may live in peace and security to advance civilisation.

### Low Temperature Research May Lecture of the Institute of Metals

THE Thirty-first Annual May Lecture of the Institute of Metals was delivered on May 28th, 1941, in the Clarendon Laboratory, Oxford, by Dr. F. Simon, F.R.S. (Reader in Thermo-dynamics in the University of Oxford), on "The Significance of Low Temperature Research." The President of the Institute, Lieut.-Col. The Hon. R. M. Preston, D.S.O., was in the chair and introduced the lecturer.

Dr. Simon began by explaining how it comes about that temperature can influence properties of matter, and showed that at low temperatures one must expect phenomena connected with small energy changes. In pre-quantum theory times no such changes could be expected, and consequently the interest in lower temperatures was mostly restricted merely to a race downwards. This changed on the advent of quantum theory which showed that the vibrational quanta in condensed matter correspond to this region of temperature. The consequent drop of the specific heat towards 0° K. is of profound influence on all properties of matter, particularly through its connection with the Third Law of Thermodynamics. This law and its implications for theory and problems of technology were then discussed, along with its corollary, the unattainability of absolute zero.

It was then shown how every phenomenon occurring in any particular temperature region can be used to reach this very region. Consequently the discovery of magnetic states of matter with very small energy differences between them led to a new method for reaching still lower temperatures than had been possible with gas liquefaction, to Debye-Giauque's magnetic method in fact. The type of information to be expected from investigations in this temperature region was discussed and similarly for the still lower region which might be reached using the nuclear paramagnetism. There is a type of phenomenon characteristic of the lowest temperatures which can occur only there, viz., that where the zero point energy is predominant, and in this connection the behaviour of liquid helium was mentioned. Finally, it appears that the low temperature region can be used to obtain results of great practical interest from model experiments: it is possible in this way to investigate phenomena inaccessible to direct experiments at high temperatures because the requirements involved, e.g., pressure or magnetic field, are then prohibitive.

The lecture will be reproduced in full in the July issue of the *Journal of the Institute of Metals*.

### Award of Institute of Metals Medal

Preceding the above lecture, the President presented the Institute of Metals Medal to Dr. C. H. Desch, F.R.S., Past President. This is the fourth award of this Institute's platinum medal, previous recipients being Sir William Bragg, F.R.S.; Sir Harold Carpenter, F.R.S.; and Dr. Paul D. Merica.

Dr. Desch, trained as an organic chemist, became Graham Young Lecturer in Metallurgical Chemistry in the University of Glasgow, and subsequently Professor Metallurgy in the Royal Technical College, Glasgow, and the University of Sheffield, and Superintendent of the Metallurgy Department of the National Physical Laboratory. Since his retirement he has been Adviser to the Iron and Steel Research Council. His text-book on "Metallography" is now in its fourth edition.

Dr. Desch is a Past President of the Institute of Metals and of the Faraday Society, and a Vice-President and Bessemer Medallist of the Iron and Steel Institute.

The low temperature mechanical properties of nickel-containing steels and alloys used in aircraft are reviewed at length in the May number of the *Nickel Bulletin*, copies of which may be obtained from The Mond Nickel Company Ltd., Grosvenor House, Park Lane, London, W.1.

### Form of Sulphur Occurrence in Blast Furnace Slag

PART of a comprehensive investigation on the mechanism of desulphurisation of iron and steel by slags includes a study of the forms in which sulphur occurs in blast furnace slag, a recent report\* on which presents data on the three sulphides most important in iron smelting, namely, ferrous sulphide, manganous sulphide and calcium sulphide. They were studied first with respect to their tendency to form dispersions in the slag. Polished specimens of sulphur-bearing slags were examined with an ultra-microscope, and the Tyndall effect was used as a means for identifying the colloid.

When ferrous sulphide was added the colour of the slag changed rapidly as the sulphide addition increased. The amount of ferrous sulphide required to form a colloid was approximately 0.03%. Slags containing about 0.4% or more of sulphur were virtually opaque. The data given indicates that ferrous sulphide is very slightly soluble in blast furnace slag of the composition studied.

Slags containing approximately 0.25% or less of sulphur as calcium sulphide were colourless but contained a colloidal phase. Further additions of calcium sulphide produced slags whose colour varied from light yellow to deep orange. All slags contained a colloidal phase that did not change noticeably as the sulphide addition was increased. Calcium sulphate did not form a colloidal phase under similar conditions, as shown by the addition of 6.0% of sulphate to the base slag. Slags containing about 3.6% or less calcium sulphide were homogeneous glass, while those containing greater amounts of sulphide were a mixture of glass and an opaque phase. This indicates that the solubility of calcium sulphide is approximately 3.6% in the standard slag at a temperature of 1,400° to 1,425° C.

Slags to which manganous sulphide had been added ranged in colour from light yellow to dark brown, and in sulphide sulphur content from 0.12 to 1.33%. All specimens contained a colloidal phase. Heat-treatment of the glassy slags below the softening point did not visibly affect the colour of the glass or the intensity of the colloid. A hypothesis of slag constitution is proposed to explain the stability of the colloidal phase in molten slag.

The dissociation pressure of manganous sulphide was determined experimentally by the method of Jellinek and Zakowski<sup>1</sup> for the temperature range 1,000° to 1,300° C., and was computed for temperatures between 1,300° and 1,600° C. At 1,400° C. a value of  $4.6 \times 10^{-2}$  mm. Hg. was obtained, showing that manganous sulphide is comparatively stable thermally at temperatures employed in melting the slags. The dissociation pressure of calcium sulphide was computed from thermodynamic data and compared with values for manganous and ferrous sulphide. The order of stability is  $\text{CaS} > \text{MnS} > \text{FeS}$ .

\* Allan E. Martin in a thesis submitted in partial fulfilment of the requirements for the degree of D.Ph., University of Minnesota, June, 1940.  
<sup>1</sup> Jellinek and Zakowski, "The Affinity of Metals for Sulphur," *Ztschr. anorg. u. allgem. Chem.*, vol. 142, 1925, pp. 1-53.

### Physicists and the War

THE importance of physics in the war effort is reflected in the maintenance of the rate of increase of membership of the Institute of Physics at the peace-time level of about one hundred per annum, noted in the recently issued Annual Report of the Institute.

The report states that the demand for trained physicists for work of National importance both in Government departments, in industry, and as technical experts with the Armed Forces continues to be urgent, and the supply is not adequate to the demand. The Institute has placed at the disposal of the Ministry of Labour and National Service all the information at its command. The Ministry of Labour and National Service is fully appreciative of the importance of physics in the war effort, and is taking all possible steps to ensure that the flow of training physicists shall be maintained.

# Avoiding Galvanic Corrosion in Light Alloy Products

By G. O. Taylor

*Many failures of metals and alloys in service are due to galvanic corrosion, and in this article the means by which this form of corrosion proceeds are discussed. Some considerations on the design of composite components are given with the object of avoiding or reducing galvanic action, and some principles are discussed, the observance of which would limit the number of failures from this cause.*

**E**LECTROLYTIC corrosion, or, as it is more familiarly known, "galvanic corrosion," is often the predominating factor leading to the premature failure in service of products made from aluminium and its light alloys. It is, however, surprising how often such failures could have been avoided by the observing of a few simple principles, particularly when the product was in the design and specification stage.

A knowledge of the mechanism by means of which galvanic corrosion proceeds is invaluable to the designer in enabling him first to specify the most suitable metal other than light alloy when confronted with the problem of producing a composite product; and secondly, in enabling him to decide the best means to adopt to ensure that the ultimate product shall be free from trouble in service.

Considering first, then, the mechanism by which electrolytic corrosion proceeds. The scientist Volta, in the year 1800, discovered that if a plate of copper and a plate of zinc were immersed in a vessel containing vinegar and were connected by a wire, the zinc plate dissolved away more rapidly than it would do if immersed alone in vinegar, and that an electric current was generated. This condition is known as electrolysis or electrolytic action, and the arrangement of two connected and dissimilar metals

connected to each other by a metallic bond (or by the non-metal carbon or graphite which for the purposes of this article may be neglected), and in the second place unless both metals are totally or partially immersed in liquid capable of conducting an electric current.

For example, if the connected plates of copper and zinc previously mentioned are immersed in pure water, no electric current will be generated, i.e., there will be no galvanic action; but if the plates are immersed in a solution of acid or alkali or in seawater, an electric current will flow and galvanic action take place, since all these liquids will conduct electricity. If, on the other hand, only one of the metals is immersed in electrolyte (conducting liquid) and the other is connected, but not immersed, galvanic action will not ensue since no electricity will be generated, neither will it ensue if both of the metals are immersed in liquid but are unconnected.

It is immaterial whether the plates are totally or partially immersed in conducting liquid. Galvanic action will occur if only the tips of the plates are immersed, and will also occur if only a film of liquid is present if this continuous and completes the electrical circuit. For instance, if a copper rivet is fastened in a zinc plate and they are exposed to sea-air, the copper rivet will eventually drop out because the zinc will be eaten away in the vicinity of the rivet

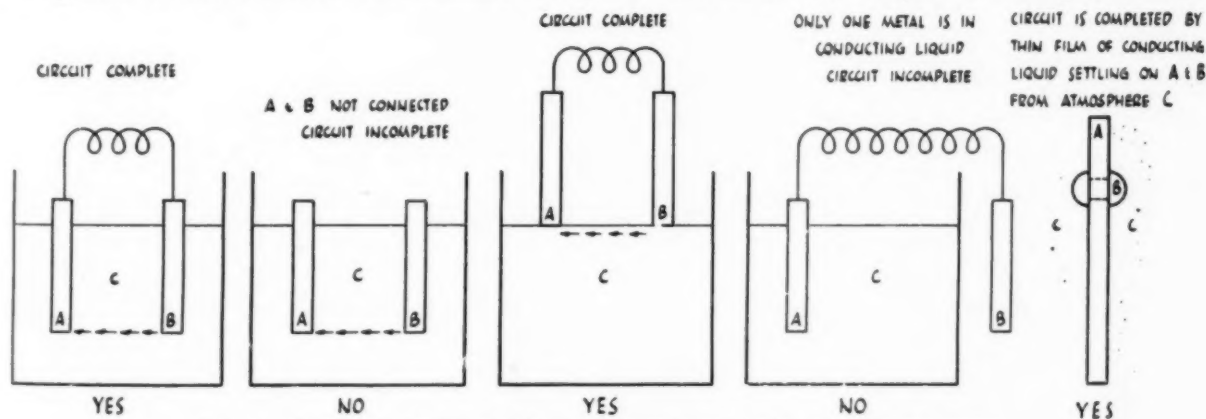


Fig. 1.—Conditions under which galvanic corrosion will and will not occur.

immersed in a solution (or electrolyte), capable of conducting electricity, is a galvanic cell.

Galvanic action should not be confused with ordinary corrosion. Corrosion is the normal disintegration of a metal by direct attack of any solution which reacts chemically with the metal. For instance, if polished steel is kept in a perfectly dry atmosphere at normal temperature it will remain unchanged, but if moisture is present in the air rust spots will quickly form, due to the reaction of iron with oxygen in the presence of water. The metal is then said to be corroding, and it is important to note that for corrosion to take place only one piece of metal need be present.

But galvanic action cannot occur unless in the first place there are present two or more dissimilar metals

due to galvanic action set up in the presence of the thin film of salt water which will at times be present on the plate.

To summarise, galvanic action can only ensue if (a) there are two dissimilar metals in "electrical" connection, and (b) if a conducting liquid is present to complete the electrical circuit. These conditions are graphically represented in Fig. 1, where the two dissimilar metals are A and B and the conducting liquid is C.

The fundamental principles which must obtain before galvanic action can occur having thus been outlined, consideration will now be given to (a) types of liquids which will fulfill the function of electrolytes (conductors of electricity), and (b) the relative degrees of galvanic action developed between aluminium and other metals.



### Liquids which will Promote Galvanic Action

Pure water is said to be a non-conductor of electricity.

Normal tap, river and lake waters are, in the majority of cases, only slightly conductive, and there is little to fear from galvanic action. But if the water is unusually "hard" or "soft" it is frequently more electrically conductive and galvanic action may ensue. This is because such waters have a dissolved mineral content which is greater than usual, and since most metallic compounds dissolved in water will increase the electrical conductivity.

For example, a composite product designed to work in ordinary water may give no trouble in one district, but in another, where the water is taken from wells or springs in peat strata, galvanic corrosion may ensue. Similarly galvanic corrosion may ensue if such products are in use with mineral waters such as occur at Buxton, Bath, Harrogate, Tunbridge and Cheltenham, since Buxton mineral waters, for instance, contain ferrous carbonate, and Bath waters dissolved salts such as magnesium sulphate and chloride.

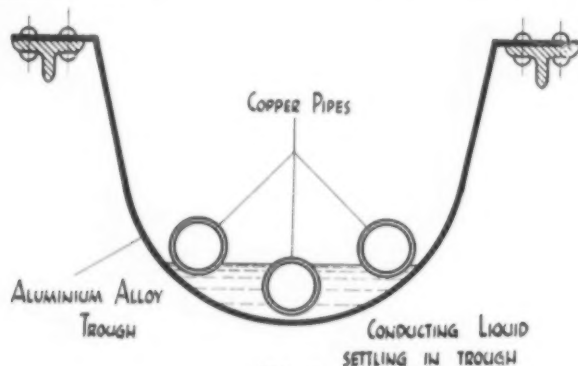


Fig. 2.

If the water is of the normal odourless and tasteless variety there is then little to be feared as to its capabilities of setting up galvanic corrosion, but if it is unusually hard or soft or has a pronounced taste or odour it is circum-spect. Fundamentally, then, galvanic corrosion demands the presence of water and of a soluble material which will increase the electrical conductivity of the water.

Perhaps the commonest example of this is in the case of seawater, where the amount of dissolved salts is sufficient to render it a fruitful source of many failures in service. It is, therefore, essential to give special consideration to the design of components required to function in sea or salt water or in sea air.

Other possible causes of contamination of water may arise from factory effluents in rivers, canals, lakes and harbours. In automobile practice the addition of some types of anti-freeze mixtures to radiator waters may lead to failure of badly designed components, and cases of severe galvanic action have also been traced to chloride flux residues left in the radiator tubes during assembly soldering operations. It is only fair to add, however, that the manufacturers of reliable grades of anti-freeze mixtures have taken precautions in the chemical constitutions of their products to avoid or minimise the possibilities of galvanic attack.

Other known sources of contamination are sulphur compounds from soot, alkali dust and condensation of acid fumes as in the vicinity of chemical works and in dense industrial regions. Acids generated in used lubricating oils can cause trouble, especially if water should accidentally find its way into the oil. A further and often overlooked source of impurity is from traces of cleaning compounds left on products during the manufacturing processes.

It will thus be seen from these few examples that although galvanic corrosion may be regarded as being unlikely in the known duties to be expected from a component, the possibility of it occurring in one of numerous

ways is always present and should be guarded against as fully as is practicable in the design stages.

### The Relative Degrees of Galvanic Action Between Aluminium and other Pure Metals

The first measure in guarding against possible galvanic action is a knowledge of the reactions to be expected when different metals are in electrical connection with aluminium and its light alloys.

It is a primary law of electricity that the rate of solution of a metal in a liquid is directly proportional to the amount of current flowing through a galvanic circuit, and that in a liquid of standard resistance the amount of current flowing is greater, the higher the potential or voltage across the circuit.

For example, in a nickel-plating bath the amount of nickel dissolved from the nickel anodes and transferred to the article being plated (which forms the other side of the galvanic circuit) is directly proportional to the number of amperes of current passing through the bath in a given time. The plater can control the number of amperes

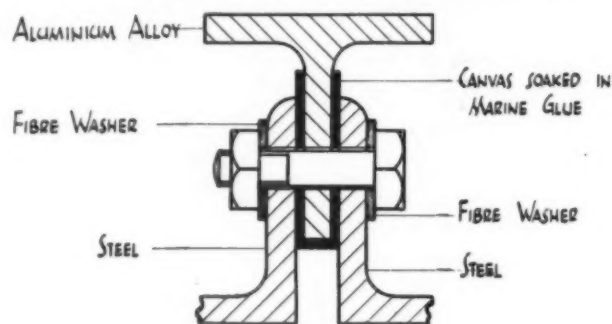


Fig. 3.

passing by raising or lowering the voltage, and can thus control at will the precise amount of nickel dissolved from the anodes and deposited on the article being plated. Actually, of course, there are other technical considerations but this familiar example will suffice to demonstrate that in the design of a composite component one of the essential considerations is to ensure that the metal coupled with the aluminium is one which will produce the minimum potential (voltage), and thus the minimum flow of current should the conditions necessary for galvanic action ensue at any time.

The metals can be arranged in a definite order known as the electro-chemical series, and although it must be appreciated that the order refers to pure metals only, and not to alloys, which, for various technical reasons beyond the scope of this article, do not always behave as might be expected, it does form a valuable primary guide. This order is as follows:

- |               |             |             |
|---------------|-------------|-------------|
| 1. Magnesium. | 5. Zinc.    | 9. Lead.    |
| 2. Aluminium. | 6. Cadmium. | 10. Copper. |
| 3. Chromium.  | 7. Iron.    | 11. Silver. |
| 4. Manganese. | 8. Tin.     | 12. Gold.   |

The above list is not the complete order, a number of metals including barium, sodium, arsenic and platinum having been omitted as unlikely to be of interest.

Aluminium is second on the list, and the further a metal is down the list, the greater the voltage or potential generated when it is coupled with aluminium in the presence of a conducting liquid. (The possible exception to this rule is zinc, which appears to exhibit an anomalous behaviour). Thus, copper, coupled with aluminium, may be expected to have a more active galvanic action on the light metal than say, iron. In passing, it is of interest to note that this order affords the explanation of why steel is so efficiently protected by zinc and cadmium, as in the case of galvanised iron sheets and cadmium-plated steel parts. Not only do the zinc and cadmium afford a mechanical protection for the steel and iron, but even if

the coating is perforated rust does not form for some time because the zinc and cadmium, being above iron in the electro-chemical series, must first be eaten away at the exposed area.

Reference to the position of magnesium relative to aluminium will be made later in this article, but it may be stated now that aluminium is always eaten away in a galvanic circuit while the metals below it remain unaffected. In other words, the aluminium is sacrificed to protect the metals below it in the order, but the rate at which it is sacrificed depends on the distance the two metals are apart in the series given.

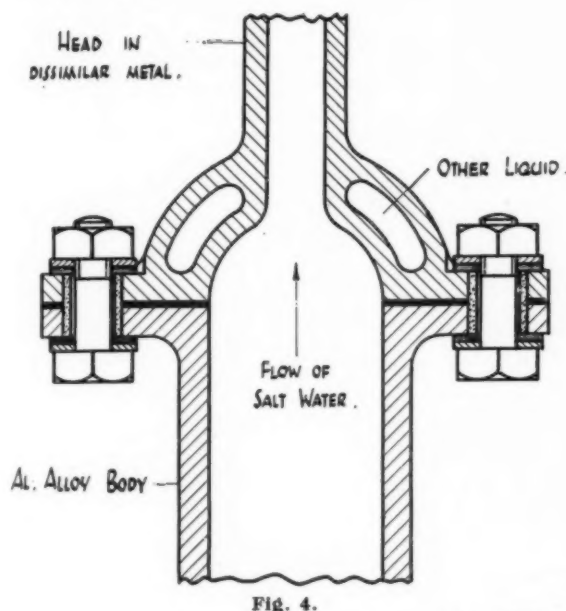


Fig. 4.

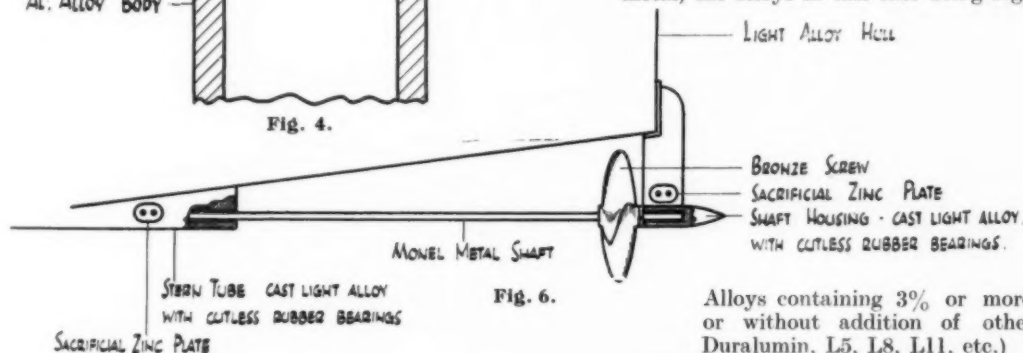


Fig. 6.

#### The Relative Degrees of Galvanic Action Between Pure Aluminium and Aluminium Alloys

This primary principle having been established, consideration will now be given to the effects introduced when mixtures of metals are made, as most of the metals are in practice used in the form of alloys one with the other.

When pure aluminium is alloyed, principally with copper, but also with small percentages of other metals as in the case of alloys of the Duralumin type, the resulting metal is depressed below aluminium in the series, as is to be expected from the addition of copper which is low down in the order. The actual extent to which it is depressed, as reckoned in millivolts, varies with the physical condition of the metal and its heat-treatment, but it is sufficiently below aluminium to render it possible to prevent the Duralumin type material from corroding in, say, sea water, if the alloy is given a coating of pure aluminium as in the case of Alclad, which consists of a Duralumin core sandwiched between outer layers of pure metal integrally bound to the core in the manufacturing process.

Although Duralumin itself will corrode in sea water, Alclad material has excellent resistance under the same conditions since, even should the pure metal coating become scratched through or otherwise damaged, corrosion of the Duralumin beneath is retarded for a considerable time until the aluminium in the vicinity of the damage has all

been eaten away or "sacrificed." This is a further excellent example of how the galvanic series can be used to advantage, as well as indicating the disadvantages which can arise from errors in design.

Similarly, if magnesium is alloyed with aluminium, there is a tendency for the resulting metal to be raised above the pure metal in the series, although the effect is not marked with additions of up to about 7% of magnesium. Thus, an alloy containing 7-10% of magnesium will exert a protective effect on pure aluminium much as pure aluminium will on Duralumin, but this fact has not yet been applied in industry. Nevertheless it is of importance, as will be demonstrated later in the article.

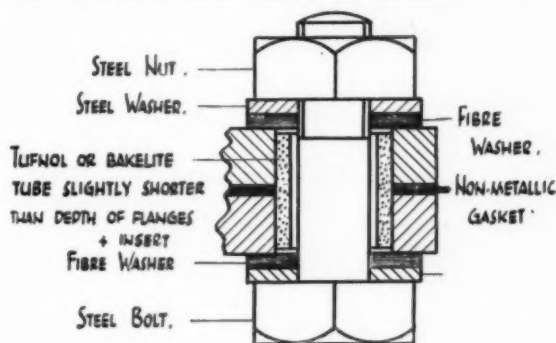


Fig. 5.

With these examples in mind there can be formulated another series useful to the designer, which shows the behaviour of aluminium alloys in relation to the pure metal, the alloys in this case being regarded as dissimilar metals.

(a) Galvanic circuits in which the probability is that the pure metal will be attacked or sacrificed when galvanic conditions are severe. Pure aluminium +

Alloys containing 3% or more of copper, with or without addition of other elements (viz., Duralumin, L5, L8, L11, etc.)

(b) Galvanic circuits in which the probability is that no galvanic action will take place.

Pure aluminium + Alloys containing up to 13% silicon or up to 7% magnesium or composite materials of the Alclad type.

It will be appreciated that in practice this sub-division into two sections will afford an approximate guide to the reactions to be expected when pure aluminium is coupled with the majority of aluminium alloys used in industry.

#### Relative Degrees of Galvanic Action Between Aluminium and its Alloys and other Metals

As previously explained, in the electro-chemical series the further down the list the pure metal is the greater the potential or voltage developed when it is coupled with pure aluminium in a galvanic circuit, and the greater the damage likely to take place on the light metal.

It is of interest, therefore, to prepare a further series which will demonstrate approximately the relation of various industrial alloys to aluminium and its alloys generally, bearing in mind that the precise degree of galvanic action will vary to some extent with the composition of the light metal, but that in all cases the light metal can be expected to be corroded if the conditions necessary for galvanic action ensue.

(1) Aluminium alloys containing 7-10% magnesium as the major constituent.

- (2) Pure aluminium: Aluminium alloys containing up to 13% silicon as the major constituent: Aluminium alloys containing up to 7% magnesium as the major constituent.
- (3) "Clad" alloys of the type Duralumin+pure aluminium, and Duralumin+copper-free Duralumin, (Due to the effect of the Duralumin core these materials may be regarded actually as being slightly below the alloys in Class 2).
- (4) Copper bearing alloys of the Duralumin and R.R. types and casting alloys such as L5, L8, L11, where the copper content usually exceeds 3%.
- (5) Wrought and cast iron: Mild steel.
- (6) Normal soft solders and "aluminium solders."
- (7) Tin and lead.
- (8) Nickel.
- (9) Brasses.
- (10) Bronzes, aluminium-bronzes and gunmetals.
- (11) Monel metal.
- (12) Copper.
- (13) Stainless steel.
- (14) Silver solder.

In the above series no reference is made to chromiums zinc and cadmium, as these are rarely used in the pure form; but they are widely used as protective coatings for other metals, and it is in this category that they require special consideration. In the electro-chemical series chromium is given immediately below aluminium, i.e., the potential difference between the two metals when coupled is small. From this it may be deduced that good quality "chromium plating" on brass or bronze or mild steel reduces the tendency of these metals to cause galvanic action on light alloys, and this fact is borne out in practice, particularly in the case of brass and bronze.

Cadmium plated steel can be recommended for contact with light alloys as the potential difference between the aluminium, and the plated metal is much smaller than if bare steel were used, and is in practice negligible.

Zinc has an anomalous behaviour, as mentioned when the electro-chemical series was discussed, and zinc-plated mild steel is actually before aluminium in the last order given, that is, if galvanised iron or plated steel is coupled with aluminium or aluminium alloy, the zinc will protect the aluminium in addition to the steel until such time as it has all been "sacrificed" in the reaction. Nevertheless, for the sake of the steel, if choice has to be made between zinc and cadmium plating in a composite steel-cum-light metal component, the cadmium is perhaps to be preferred, since there is little potential generated in the circuit, and the steel will probably be protected for a longer time.

#### Some Considerations on the Design of Composite Components to Avoid Galvanic Action

In the design of light metal components of a composite type, where the light metal is required to work in conjunction with a dissimilar metal, much can be done to avoid possible failure from galvanic action if two simple principles are observed.

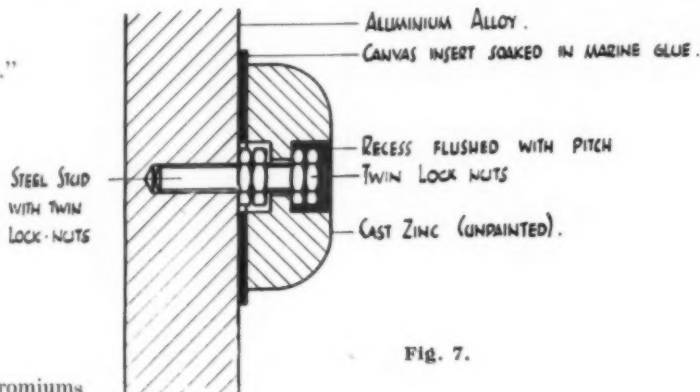
The first principle is that where the designer has a choice between several metals, if other considerations are equal, the one should be chosen which is as near as possible to the light metal in the various series already given. This will ensure that, should galvanic conditions ensue, the potential generated, and therefore the damage likely to be caused to the light metal, will be at a minimum.

The second principle is that, bearing in mind the fundamental fact that galvanic action is due to the flow of

electricity from one metal to another, precautions should be taken to break up the circuit as much as possible by insulating the metals one from the other.

There is also a third and minor principle which cannot be applied in all circumstances, which is the use of a third metal to be deliberately sacrificed to protect the light alloy, but this will be referred to later.

Considering now methods of carrying out insulation, it is obvious that the procedure will vary greatly in different types of components, but there are a number of salient factors worthy of note:



- (a) A good coating of paint or enamel will reduce the possibility of galvanic action by restricting the free passage of conducting liquid to the metal surfaces.
- (b) Surfaces in contact but first coated with a material of the engine jointing compound type will not react so readily as in the case where no jointing material is present and liquid can penetrate into the interstices between parts.
- (c) The presence of rubber washers, canvas inserts soaked in jointing compound, fibre washers, bakelite materials, etc., between the dissimilar metals is advantageous in restricting the area of the metals in contact.
- (d) Anodising and subsequent lanoline impregnation of the aluminium alloy part is advantageous, as the conducting liquid cannot penetrate readily through the oxide film to carry current to the light metal.

With these salient points in view a number of composite constructions will be discussed and methods of preventing galvanic action illustrated.

Considering, first, the simple case of a trough-like aluminium alloy sheet part along which are running copper pipes, say, for the purpose of pumping oil. As will be seen in Fig. 2, there is a possibility that at some time conducting liquid may condense into, or otherwise settle in, the trough, in which case corrosion of the aluminium alloy due to galvanic action may be expected.

In such circumstances the remedy is simple, and would consist in (a) anodising and painting the aluminium alloy part, and (b) wrapping the copper tubes in electricians, insulating tape, and then coating well with varnish prior to fixing in position. In many cases the precaution (b) only would suffice.

Taking now another simple case where it is necessary for some purpose to bolt an aluminium alloy tee-section between two steel plates, and in which the assembly will be required to work under conditions where it is known that galvanic action is possible. A convenient procedure to adopt in this case would be as in Fig. 3.

A strip of thin canvas is folded over the end of the tee and fixed into position with an adhesive. When the

(Continued on page 66.)



# Note on the Resistance to Furnace Atmospheres of Heat-Resisting Steels\*

By A. G. Quarrell, Ph.D., F.Inst.P.

(THE UNIVERSITY OF SHEFFIELD).

*The application of the high-temperature method of electron diffraction to thin oxide films formed on a heat-resisting steel has shown that at temperatures up to 950° C. the oxide has a spinel structure. This is possessed by a large number of oxides of the general type  $XO.Y_2O_3$ , and is both exceedingly flexible and inherently stable. It is suggested that the oxidation resistance of heat-resisting steels is largely due to the formation of a stable spinel.*

IN the Second Report of the Alloy Steels Research Committee, Section IV.,<sup>2</sup> an account was given of a new technique of electron diffraction for examining iron-oxide films at the temperature of formation. It was shown that the  $Fe_3O_4$ , which was stable below about 400° C., was converted to  $FeO$  on heating above 500° C., and this oxide was stable up to the critical point of the ingot iron. Between 400° and 500° C., either  $Fe_3O_4$  or  $FeO$ , or a mixture of the two oxides, was obtained, depending upon the thickness of the film. Between 515° C. and the  $A_3$  change point the initial film consisted of a new hexagonal oxide bearing an intimate structural relationship with the underlying iron lattice, but further oxidation led to the formation of normal  $FeO$ . Above the  $A_3$  point the oxide was  $Fe_3O_4$ . On cooling to room temperature, the oxide invariably reverted to  $Fe_3O_4$ , and therefore at least two transformations occurred in the oxide film on heating to, or cooling from, 950° C. Since there is no simple relationship between the  $FeO$  and  $Fe_3O_4$  structures, these transformations must necessarily cause some disruption of the oxide film and so facilitate the passage of oxygen from the atmosphere to the underlying iron surface, thus leading to further oxidation.

The high-temperature technique has since been applied between room temperature and 950° C. to a heat-resisting steel of the following composition:—

Carbon	Manganese	Silicon	Nickel	Chromium	Molybdenum
0.47%	0.72%	1.7%	12.9%	13.1%	3.1%

Whereas with the ingot iron a single volume of 3 c.c. of air sufficed to cause the formation of an oxide film which gave a well-defined diffraction pattern, at least 10 or 20 volumes were necessary with the heat-resisting steel. It was found that at all temperatures of formation and examination, for films of various thicknesses up to that corresponding to 100 volumes of air, the oxide film gave an electron-diffraction pattern corresponding to a spinel structure, but with very small crystal size. The spinel structure with a complicated cubic unit cell is possessed by a large number of compounds including, for example,  $Fe_3O_4$ . Moreover, the lattice parameters of the different spinels differ only slightly from one another, and therefore it is not possible to decide from electron-diffraction data the exact nature of the spinel observed on the heat-resisting steel. As will be shown later, it is probable that any attempt to assign a particular composition to the spinel oxide would be doomed to failure, but it can safely be assumed that it is not  $Fe_3O_4$ , since the experiments on ingot iron show that this is stable only below 450° C. and above 900° C. It was at first thought that selective oxidation had occurred and that a film of nickel chromite,  $NiO.Cr_2O_3$ , had been formed, but a consideration of the various spinel structures already known to exist suggests an alternative and more interesting explanation.

The spinel structure is possessed by a very large number of oxides of the type  $XO.Y_2O_3$ , where, according to classical conceptions, X is a divalent and Y a trivalent metal atom. In addition, natural spinel minerals are found in which the X positions on the lattice are shared among two or more metals, not always in the same proportions, e.g., chromite ( $Fe,Mg$ )  $O.Cr_2O_3$ , and jacobite, ( $Mg,Mn,Fe$ )  $O.Fe_2O_3$ . More recently, in order to explain the abnormal intensities observed in the X-ray patterns from spinels it has been found necessary to assume<sup>3</sup> that the X atoms may even change places with those normally occupying the Y positions. Indeed, spinels have been observed in which the Y positions are all occupied by atoms which are normally regarded as divalent, e.g.,  $TiO.Zn_2O_3$ <sup>4</sup> and  $SnO.Zn_2O_3$ .<sup>5</sup> Spinel has already been observed with molybdenum, cadmium, cobalt, copper, iron, magnesium, manganese, tin, titanium or zinc in the X position, and silver, aluminium, cobalt, chromium, iron, gallium, indium, magnesium, manganese, nickel, vanadium or zinc in the Y position. The spinel structure is also possessed by both  $\gamma$ - $Fe_2O_3$  and  $Fe_3O_4$ .

The foregoing facts make it clear that the spinel structure is exceedingly flexible, and at the same time it must be inherently stable, otherwise the introduction of a new type of metal atom into the lattice would cause a change in dimensions or even a conversion to a different structure. The lack of protection afforded by the spinel  $FeO.Fe_2O_3$  on ingot iron and plain carbon steels must be regarded as exceptional and attributed to the fact that both the X and Y positions are occupied by iron atoms, thus making it possible for the lattice as a whole to be converted to the lower oxide  $FeO$ .<sup>6</sup> With the more general type of spinel, containing at least two different metals, a corresponding change is impossible, and therefore the structure should be stable over a much wider range of temperature. Consequently, on heating or cooling there will be no disruption of the lattice and there will be no time at which oxygen will be able to pass freely through newly developed cracks to oxidise the underlying metal. An example of a truly protective spinel film is afforded by nickel-chromium alloys. The oxide formed on an 80/20 nickel-chromium alloy has been shown by electron diffraction to consist of  $NiO.Cr_2O_3$ , and there can be no doubt that the spinel affords excellent protection against corrosion in this case.

On the assumption, therefore, that a spinel oxide containing two different metals does, under suitable conditions confer protection, it is possible to build up a theory to explain the resistance to furnace atmospheres offered by heat-resisting steels. Consider what happens when the amount of alloying elements—say, nickel and chromium—

<sup>3</sup> Wyckoff, "Supplement to 'The Structure of Crystals,'" p. 69. New York, 1935: Reinhold Publishing Corporation.

<sup>4</sup> Holgersson and Herrlin, *Zeitschrift für anorganische Chemie*, 1931, vol. 198, p. 69.

<sup>5</sup> Barth and Posnjak, *Zeitschrift für Kristallographie*, 1932, vol. 82, p. 325.

<sup>6</sup> Even  $FeO.Fe_2O_3$  affords protection in certain temperature ranges, e.g., blueing of boilers.

\* Paper No. 2/1941 of the Alloy Steels Research Committee, Iron and Steel Institute, 1941 (advance copy).

<sup>2</sup> Iron and Steel Institute, 1939, Special Report No. 24.

is gradually increased from zero, and oxidation occurs in air at 950° C. With pure iron the oxide formed will consist of  $\text{Fe}_3\text{O}_4$ , and even when small quantities of nickel and chromium are present the oxide will still behave as if it were  $\text{Fe}_3\text{O}_4$  and will be converted to  $\text{FeO}$  on cooling below about 900° C. Eventually, with higher contents of the alloying metals, the nickel and chromium will take control and stabilise the spinel structure. The steel will then show considerable resistance to oxidation, although, of course, its mechanical properties at high temperatures may not be satisfactory. In order to obtain the necessary mechanical properties at high temperatures it may be necessary to add other alloying elements, and the question arises as to whether these additional elements will have a deleterious effect upon the corrosion resistance. As will be seen from the list of already investigated spinels (Table I.), however, any metal used or likely to be used as an alloying element in a heat-resisting steel can take up either the X or Y position in the spinel lattice, and it is at least highly probable that, once the spinel has been stabilised, it can accommodate any of the metals likely to be encountered. If this view is correct, the composition of the oxide film on a heat-resisting steel will depend upon the composition of the steel, and no exact formula corresponding to  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  can be assigned to it.

TABLE I.

OXIDES AND SULPHIDES KNOWN TO POSSESS A SPINEL STRUCTURE.

Oxides		
$\text{CrO} \cdot \text{Cr}_2\text{O}_3$	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$\text{SnO} \cdot \text{Co}_2\text{O}_3$
	$\text{MgO} \cdot \text{CO}_2\text{O}_3$	$\text{SnO} \cdot \text{Mg}_2\text{O}_3$
$\text{CdO} \cdot \text{Fe}_2\text{O}_3$	$\text{MgO} \cdot \text{Cr}_2\text{O}_3$	$\text{SnO} \cdot \text{Zn}_2\text{O}_3$
	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	
$\text{CoO} \cdot \text{Al}_2\text{O}_3$	$(\text{Mg}, \text{Mn}, \text{Fe})\text{O} \cdot \text{Fe}_2\text{O}_3$	$\text{TiO} \cdot \text{Fe}_2\text{O}_3$
$\text{CoO} \cdot \text{Co}_2\text{O}_3$	$\text{MgO} \cdot \text{Ga}_2\text{O}_3$	$\text{TiO} \cdot \text{Mg}_2\text{O}_3$
$\text{CoO} \cdot \text{Cr}_2\text{O}_3$	$\text{MgO} \cdot \text{In}_2\text{O}_3$	$\text{TiO} \cdot \text{Mn}_2\text{O}_3$
$\text{CoO} \cdot \text{Fe}_2\text{O}_3$		$\text{TiO} \cdot \text{Zn}_2\text{O}_3$
$\text{CoO} \cdot \text{Mn}_2\text{O}_3$	$\text{MoO} \cdot \text{Ag}_2\text{O}_3$	
		$\text{ZnO} \cdot \text{Al}_2\text{O}_3$
$\text{CuO} \cdot \text{Al}_2\text{O}_3$	$\text{MnO} \cdot \text{Al}_2\text{O}_3$	$\text{ZnO} \cdot \text{Co}_2\text{O}_3$
$\text{CuO} \cdot \text{Co}_2\text{O}_3$	$(\text{Mn}, \text{Co})\text{O} \cdot (\text{Co}, \text{Mn})_2\text{O}_3$	$\text{ZnO} \cdot \text{Cr}_2\text{O}_3$
$\text{CuO} \cdot \text{Fe}_2\text{O}_3$	$\text{MnO} \cdot \text{Cr}_2\text{O}_3$	$\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
	$\text{MnO} \cdot \text{Fe}_2\text{O}_3$	
$\text{FeO} \cdot \text{Al}_2\text{O}_3$		
$\text{FeO} \cdot \text{Cr}_2\text{O}_3$	$\text{NiO} \cdot \text{Al}_2\text{O}_3$	
$(\text{Fe}, \text{Mg})\text{O} \cdot \text{Cr}_2\text{O}_3$	$(\text{Ni}, \text{Co})\text{O} \cdot (\text{Co}, \text{Ni})_2\text{O}_3$	
$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	$\text{NiO} \cdot \text{Cr}_2\text{O}_3$	
$\text{FeO} \cdot \text{V}_2\text{O}_5$	$\text{NiO} \cdot \text{Fe}_2\text{O}_3$	
Sulphides		
$\text{CdS} \cdot \text{S}_2$	$\text{CuS} \cdot \text{CoS}_2$	$\text{NiS} \cdot \text{Ni}_2\text{S}_3$
$\text{CoS} \cdot \text{Co}_2\text{S}_3$	$\text{MnS} \cdot \text{CrS}_2$	$\text{ZnS} \cdot \text{Cr}_2\text{S}_3$
$(\text{Co}, \text{Ni})_2\text{S}_4$		

In practice, a heat-resisting steel is usually subjected to furnace atmospheres containing sulphur, and therefore it might be thought that the foregoing observations can have little bearing on the behaviour of such steels under industrial conditions. Further reference to the list of spinel structures (Table I.) shows that mixed sulphides can also form spinels. It is true that these sulphides have a rather larger unit cell than the corresponding oxides, but nevertheless it is probable that in a sulphurous atmosphere the spinel layer formed on a heat-resisting steel will be a mixed sulphide-oxide spinel. In other words, it is possible to visualise a spinel structure which can accommodate not only the various metals contained in the steel but also the oxygen and sulphur in the proportions in which they occur in the furnace gases. Such a spinel would be expected to withstand cyclic temperature changes without breakdown of the lattice, and, furthermore, changes in the composition of the furnace gases might quite well be counterbalanced by the interchange of sulphur and oxygen atoms. If this were so, then the spinel would automatically adopt a composition which would be in equilibrium with the atmosphere, without at the same time breaking up or allowing excessive corrosion.

It should be noted that the stable spinel, whether oxide or oxide-sulphide, could contain a large proportion of iron, provided that sufficient alloying constituents were present to prevent the reversion to  $\text{FeO}$  on cooling.

One would not expect to observe a great difference in the protection afforded by spinels of different compositions, but the stability of the spinel at high temperatures would be determined by its composition, and it is from this point of view that the composition of a heat-resisting steel may possibly be critical in so far as oxidation resistance is concerned.

It is known from experience that protective oxide films are invariably amorphous or have a very small crystal size as was the case with the heat-resisting steel examined. Heat-resisting alloys containing fairly large proportions of aluminium have proved very successful, and there is a tendency to attribute this to the formation of an amorphous aluminium-oxide film such as is known to be formed on aluminium, and which is probably the most protective oxide film known. That this explanation is probably incorrect can be seen from the work of Preston and Bircumshaw,<sup>7</sup> who showed that the amorphous aluminium oxide becomes crystalline, and therefore loses much of its protective power, at about 700° C. On the other hand, aluminium may be regarded as a powerful stabilising element, since it forms spinel oxides with cobalt, iron, manganese or nickel in the X positions, and it may well be that heat-resisting steels containing aluminium owe their corrosion resistance to the formation of a particularly stable spinel oxide film.

Many heat-resisting alloys contain a large percentage of silicon, and in this case the protective layer could well be amorphous. Amorphous silica is stable and protecting over a remarkable range of temperatures, as is indicated by a series of electron diffraction experiments carried out by Finch.<sup>8</sup> On removal from the electric arc furnace in which they are made, silicon-carbide crystals are found to be coated with a thin, invisible amorphous silica film, which protects the crystal from further oxidation. If the silica film is removed and the crystal is then heated gently in a Bunsen flame, it immediately becomes coated once more with a similar invisible film. It can therefore be concluded that the amorphous silica film is extremely protective and at the same time is stable even at very high temperatures.

The author thanks Professor J. H. Andrew, D.Sc., for much valuable advice and criticism, and the members of the Alloy Steel Research Committee for helpful and stimulating discussion.

<sup>7</sup> Preston and Bircumshaw, *Philosophical Magazine*, 1936, vol. 22, p. 654.  
<sup>8</sup> Finch, *Journal of the Chemical Society*, 1938, p. 1140.

## Meteorites in the U.S.S.R.

THE Academy of Sciences of the U.S.S.R. claims to have one of the largest collections of meteorites in the world, numbering 93 specimens found in the Soviet Union and 55 specimens which have fallen in other countries. The aggregate weight of the Academy's collection is 4,189 lbs. The collection includes some unique specimens, of which the most valuable is the "Pallas Iron." This is the largest meteorite in the U.S.S.R., weighing more than half a ton. It was found on the banks of the River Zenisei in 1749, and in 1771 was transported to St. Petersburg. Although at that time science denied the possibility of stones falling to earth from cosmic space, Pallas, who brought the iron mass to St. Petersburg, was convinced that it was a meteorite.

The Pallas meteorite laid the foundation of the remarkable collection now formed. Another included, which is not less interesting, is the "Boguslavka" meteorite. This is claimed to be the largest iron meteorite in the world observed falling by eye witnesses. It fell in one of the far eastern districts of Russia in October, 1916, and in two parts, weighing 439 lbs. and 121 lbs. respectively.

# Dust Explosion Hazards in Plants Producing or Handling Aluminium Magnesium and Zinc Powder

*Early investigators believed that only the carbonaceous dusts formed explosive mixtures with air, and it is only during comparatively recent years that the explosibility of certain metal and mineral dusts has been recognised. Study of this problem emphasises the need for development of some effective method of fighting fire and preventing explosions in plants producing or handling aluminium, magnesium or zinc powder. A summary of laboratory tests is given covering the explosibility of certain metal dusts, with brief reference to their uses and methods of manufacture.*

**A**LTHOUGH extensive research has been carried out to determine the factors affecting the explosibility of carbonaceous dusts, and much has been published on coal dust and grain dust explosions, recent reports of loss of life and property in explosions of metal dusts emphasise the lack of information on the extent of the dust explosion hazard in plants manufacturing or handling aluminium, magnesium or zinc powder, as well as other metal and mineral dusts. Early investigators believed that only the carbonaceous dusts formed explosive mixtures with air, and it was not until the beginning of the present century that the explosibility of certain metal and mineral dusts was generally recognised.

Many vague references to metallic dust explosions are found in the literature, but very little information seems to be available on the extent of the hazard, the number of explosions, or the amount of loss caused by explosions in plants handling metallic or mineral dusts or powders other than those of a carbonaceous nature. To indicate the extent of the hazard a summary of laboratory tests is given by H. R. Brown\* covering the explosibility of certain metal dusts, with brief experience of their uses and methods of manufacture.

Many investigators have conducted laboratory tests with aluminium powder, and some information is available on the explosive properties of magnesium and zinc. Some of the work on ignition temperatures, explosive limits, pressures produced, and any peculiarities noted in connection with these investigations is briefly reviewed.

## Aluminium Powder

Aluminium powder is used widely in the manufacture of paint, in printing and the preparation of aluminium-coated paper, in the manufacture of fireworks and flashlight powder, for protection of balloon and dirigible fabric, in welding compounds, and to a small extent in the manufacture of plastics and other materials where special decorative effects are desired.

Some aluminium powder is produced by the atomisation process, in which the molten metal passes over a stream of air or gas; but such material is not suitable for printing or use in paint owing to the shape of the particles, and most of the aluminium powder now manufactured is prepared by stamping. In this process aluminium scraps or sheets are placed in the stamp mills, where steel hammers reduce the aluminium to powder or fine flakes, practically all of which pass through a 200-mesh sieve.

There is some variation in ignition temperatures of aluminium powder as determined by different investigators. Stockmeier (1) gives the ignition temperature as 480°–490° C., but states that the finest aluminium powder may ignite at 230° C. Leighton (2) failed to get an ignition of either 50- or 100-mg. samples in the Clement-Frazier

apparatus at temperatures of 800°–1,200° C., but was able to ignite it at 800° C. when a larger source of ignition was used. In a publication of the engineering department of the Factory Insurance Association, Hartford, Conn. (3) the ignition temperature of aluminium dust is given as 1,697° F. (925° C.) Trostel and Frevert (4) reported ignition of aluminium dust in the Clement-Frazier bomb with the glower at a temperature of 925° C. Ignitions by an induction-coil spark at 6.5 volts and 3 amperes were reported also by Trostel and Frevert. Beyersdorfer (5) gives 485° C. as the ignition temperature of aluminium powder and 230° C. as the ignition temperature of aluminium grindings. Ritter (6) refers to mechanical work in the form of shock, collision, or friction, and mechanically produced heat and sparks as sources of ignition and states that such ignitions have been known to occur. The author has ignited aluminium-dust clouds by sparks produced when a piece of steel was held in contact with a grinding wheel.

Explosive limits for aluminium dust as reported by different investigators vary widely. From tests with a new apparatus which they developed and which they claim produces a uniform distribution of the sample Mason and Taylor (7) set the lower limit between 40 and 50 mg. per litre. Bauer (8) reported the lower limit as 432 mg. per litre. Trostel and Frevert (4) reported ignitions of aluminium dust at concentrations of 7 mg. per litre when the glower or electric arc was used as a source of ignition and 13.7 mg. per litre when the induction spark was used. Matla (9) reported the lower explosive limit for aluminium dust as 28 mg. per litre. A description of the apparatus and method used by Bauer (8) indicates that some of the dust used in the tests may not have been in suspension, and the concentration cited would accordingly be too high. Gliwitzky (10) reports 0.04 gram, or 40 mg. per litre as the approximate minimum explosive concentration of aluminium dust.

All investigators mention increases in pressure as the concentration is increased, but with considerable variation when the particle size of the sample differs. Within the range used by most of the investigators the pressure rise is almost directly proportional to the concentration when similar dust is used, but Mason and Taylor (7) call attention to the fact that approximately 300 mg. of aluminium

2 Leighton, Alan. "The Inflammability of Aluminium Dust." *Bureau of Mines Tech. Paper* 152, 1918, pp. 10-11.

3 Factory Insurance Association, "Determination of Dust-Explosion Possibilities." Special Hazard Study 4, Hartford, Conn., January, 1940, p. 8.

4 Trostel, L. J., and Frevert, H. W. "The Lower Limits of Concentration for Explosion of Dust in Air." *Chem. and Met. Eng.*, vol. 30, 1924, pp. 141-146.

5 Beyersdorfer, P., and Braun, L. "Über den Begriff Feuergefährlichkeit" (The Fire Hazard Situation). *Ztschr. Tech. Physik*, vol. 9, No. 1, 1928, pp. 17-19.

6 Ritter, F. "Über die Ursachen der Entzündung des Aluminiumstaubes bei der Herstellung" (The Causes of Ignition of Aluminium Dust During Manufacture). *Ztschr. Ver. deut. Ing.*, vol. 74, 1930, pp. 145-148.

7 Mason, R. B., and Taylor, C. S. "Explosion of Aluminium-Powder Dust Clouds." *Ind. Eng. Chem.*, vol. 29, No. 6, 1937, pp. 626-31.

8 Bauer, G. "Einiges über Staubeexplosionen" (Dust Explosions). *Ztschr. ges. Schiess u. Sprengstoff*, vol. 13, 1918, pp. 272-273.

9 Matla, W. P. M. "Dust Explosions." *Rec. trav. chim.*, vol. 55, 1936, pp. 173-91.

10 Gliwitzky, W. "Messung des Druckverlaufs bei Aluminiumstaub Explosionen." (Measurement of Pressure in Aluminium-Dust Explosions). *Ztschr. Ver. deut. Ing.*, vol. 80, 1936, pp. 687-92.

\* Bureau of Mines Information Circular 7148. United States Department of the Interior, Pittsburgh, Pa.

1 Stockmeier, H. "Über die Explosionen in der Aluminiumbronzefarben-Industrie" (Explosions in the Aluminium-Bronze Industry). *Ztschr. angew. Chem.*, vol. 19, II, 1906, pp. 1665-68.



powder will consume all of the oxygen in 1 litre of air at room temperature and pressure. Gliwitzky<sup>(10)</sup> reports that the maximum pressure increases, and the time required to reach the maximum decreases as the size of the particle is decreased. For particles of sizes 1.3, 0.6, and 0.3 microns the pressures were 7.7, 8.6, and 10.6 atmospheres and the time was 0.06, 0.03, and 0.012 second, respectively, with a concentration of 0.7 gram of dust per litre. The maximum pressure obtained in aluminium dust and air explosions was 11.6 atmospheres. Edwards and Leinbach<sup>(11)</sup> determined the maximum pressure, the average rate of pressure rise, and the maximum rate of pressure rise in a series of tests with aluminium dust at concentrations of 100 and 500 mg. per litre. The maximum pressure recorded was 23 pounds per square inch with the 100-mg. concentration and 40 pounds per square inch with the 500-mg. concentration. At these concentrations the average rate of pressure rise was 170 and 240 pounds per square inch per second, and the maximum rate of pressure rise was 513 and 724 pounds per square inch per second respectively. It is this rapid rate of pressure rise that makes the control of aluminium dust explosions by the release of pressure through building vents, such as those applicable to carbonaceous dusts, exceedingly difficult. The Factory Mutual Laboratories<sup>(12)</sup>, in recent tests made with a 200-mesh sample of aluminium dust and an improved method of dispersing the dust, report pressures as high as 56 pounds per square inch, while corn starch, considered one of the most explosive carbonaceous dusts, tested under the same conditions, produced 30 pounds per square inch.

#### Peculiarities Noted in Investigations

Zimmerman<sup>(13)</sup> reports that flash lamps containing aluminium foil and oxygen can ignite the aluminium foil in similar bulbs at a distance of 10 to 20 cm. through an interposed screen of moistened cellophane. Wolf<sup>(14)</sup> claims that where aluminium foil or powder is produced it can be ignited not only by fire or sparks but also by the effect of light. Several investigators state that the inflammability of aluminium depends on the surface exposed. Reference is made in a number of articles to the decomposition of water into hydrogen and oxygen by aluminium powder and the possibility of ignition and explosion of the hydrogen. Decomposition may occur at temperatures as low as 30° C. Stockmeier<sup>(1)</sup> also calls attention to the increased explosion hazard if oxygen carriers are present. Ordinarily stable under friction, aluminium powder explodes violently with gentle rubbing after the addition of potassium chlorate. Even in a coarsely divided state amalgamated aluminium ignites immediately upon exposure to air.

#### Magnesium Powder

Magnesium, a light, brilliant, silver-colored metal just a little softer than aluminium, has received considerable attention in recent years because of its increased use in construction where lightness with strength is desirable, as in the aircraft industry. Although the explosion or fire hazard is present in the machining of castings and the storage or handling of turnings and scrap, the principal danger occurs in the manufacture and use of the powder.

The principal use of magnesium powder is in flashlight powder, fireworks, flares, star shells, illuminating shells, tracer bullets, and the production of smoke screens. In such uses it may be combined with aluminium or other metallic powders. In powdered form magnesium is also used as plant food for tobacco, potatoes, cotton, etc.

Magnesium powder is produced in different types of mills and ranges in size from 30-mesh to 265-mesh or finer.

The 200-mesh or finer sizes usually are specified for flashlight powder. In addition to magnesium powder, commercial flashlight powder may contain barium nitrate potassium chlorate, or other materials. All magnesium in the United States is produced by one company, but about 30 other companies are licensed to fabricate it, and a number of these manufacture the powder.

The ignition temperature found by different investigators varies for magnesium as it did for aluminium. The literature available is more limited, and methods of determining the ignition point are not always given. The most complete report is given by Brown<sup>(15)</sup>. The method of making the tests is described in detail, and the data show that magnesium in the form of small pieces of ribbon 0.2 by 3.0 mm. ignited at 507° C. A report on the inflammability of magnesium by the Factory Mutual Laboratories<sup>(12)</sup> states that where an entire piece of the metal can be raised to a temperature of about 499° C., ignition will take place. In an article on the magnesium industry Gann<sup>(16)</sup> points out that the ignition temperature drops rapidly as particle size decreases, but gives no ignition temperature for the fine dust. It is known that metallic or electric sparks have produced ignitions of magnesium powder, and the dust ignites readily in the Clement-Frazer apparatus with the coil at 900° to 1,200° C. Although no tests have been reported on the determination of the ignition temperatures of magnesium and aluminium dust clouds under similar conditions, comparison of the data available indicates that the fine magnesium powders may be ignited at temperatures below those required to ignite the finer sizes of aluminium powder.

Little information is available in the literature searched on the explosive limits of magnesium powder, and about the only means of determining approximate limits is by comparison with other dusts. In the most recent tests of magnesium powder by the Factory Mutual Laboratories<sup>(12)</sup>, pressures of 14 pounds per square inch were produced at concentrations of only 50 mg. per litre or 50 ounces per thousand cubic feet. This would indicate that the lower limit probably is well below the limit determined by several investigators for aluminium powder—40 mg. per litre. The curve drawn from pressures obtained in magnesium-dust explosions at different concentrations flattens and shows little or no increase in pressure at concentrations above 312 mg. per litre. As no decrease in pressure was noted when the concentration was increased to 380 mg. per litre, it was not possible even to approximate the upper limit. Edwards and Leinbach<sup>(11)</sup> obtained explosions and recorded high pressures at concentrations of 500 mg. per litre. Improved methods now being developed for obtaining uniform concentrations of dust in air undoubtedly will allow more accurate determination of explosive limits.

Extraordinarily high pressure develops in explosions of magnesium powder or dust from magnesium alloys. Edwards and Leinbach<sup>(11)</sup> report a pressure of 40 pounds per square inch in tests at a concentration of 500 mg. per litre and a maximum rate of pressure rise at the same concentration of 788 pounds per square inch per second. In tests made by the Factory Mutual Laboratories<sup>(12)</sup> magnesium dust developed a pressure of 68 pounds per square inch, or nearly double the pressure of aluminium or cornstarch under similar conditions.

Although magnesium is not attacked by water at room temperature, it is slowly decomposed by water at 100° C. with the formation of hydrogen. Dilute acids may cause a violent evolution of hydrogen. In machining metal parts surrounded by magnesium or magnesium-alloy castings, sparks or heat produced by the machine tool may ignite the dust or chips and cause a hot fire. In one instance

<sup>11</sup> Edwards, P. W., and Leinbach, L. R. "Explosibility of Agricultural and Other Dusts as Indicated by Maximum Pressure and Rate of Pressure Rise." *U.S. Dept. of Agriculture Tech. Bull.* 490, 24 pp. (esp. p. 13).

<sup>12</sup> Factory Mutual Laboratories, Associated Factory Mutual Fire Insurance Companies, 184, High Street, Boston, Mass. Private letter concerning unpublished laboratory test reports.

<sup>13</sup> Zimmerman, W. "Eine Eigenartige Wirkung von Photographischen Blitzlicht" (Peculiar Effect of Photographic Flash Lamps). *Naturwissenschaften*, vol. 18, 1930, p. 867.

<sup>14</sup> Wolf, Hans. "Über zwei wenig bekannte Explosionsursachen" (Two Little-known Explosion Sources). *Chem. Ztg.*, vol. 54, 1930, p. 796.

<sup>15</sup> Brown, C. R. "The Determination of the Ignition Temperatures of Solid Materials: Thesis for Degree of D.Sc." The Catholic University of America, Washington, D.C., 1934, 83 pp. (esp. pp. 45, 46, 57, 61, 66).

<sup>16</sup> Gann, John A. "The Magnesium Industry." *Ind. Eng. Chem.*, vol. 22, No. 7, July, 1930, pp. 694-700.

reported, sparks from a grinding wheel ignited magnesium dust and caused an explosion that killed three men and injured several others.

### Zinc Powder

Zinc powder is used principally to precipitate and recover gold and silver from cyanide solutions but also is used largely in dye plants. It may be mixed with aluminium, magnesium and other powders in making fireworks and smoke screens. A limited amount is used for plant food. Practically all zinc dust is produced by redistillation of zinc dross and slab zinc, and the product as marketed usually is very fine. More than 99% of the powder in the samples tested passed through a 200-mesh screen.

The amount of information available on the explosibility of zinc dust is quite limited. One report indicates that the powder ignites at about 360° C. Owing to its weight, zinc dust does not readily form a cloud in air, but it can be ignited easily in the Clement-Frazer apparatus either with the coil at 900° to 1,200° C. or with the magnesium-barium-peroxide pellet, which is calculated to produce a temperature of about 1,800° C.

One investigator reports that he obtained an explosive mixture by blowing 4 grams of zinc dust into suspension in an open-end tube by releasing about 33 cubic inches of air at 10 to 50 cm. of mercury. Not enough additional data are given for even an estimate of the actual concentrations obtained in such tests. Edwards and Leinbach<sup>(11)</sup> obtained ignitions at concentrations of 100 and 500 mg. per litre. Later tests indicate that owing to the weight of the dust and the method used to throw it into suspension, the concentration at the point of ignition may have been below that indicated.

In a few reports available on explosion tests with zinc powder the earlier results indicate that the pressures developed are comparatively low. Edwards and Leinbach<sup>(11)</sup> report pressure of only 3 pounds at a concentration of 100 mg. per litre and 8 pounds at the 500 mg. concentration. One other report gives a pressure of 4.5 pounds at a concentration of 5 grms. per litre of air. Recent developments indicate that the low pressures obtained undoubtedly were due to unsatisfactory methods of producing a uniform concentration of zinc dust in air. With an improved method of producing the dust and air mixture in the Clement-Frazer apparatus, the Factory Mutual Laboratories<sup>(12)</sup> recently obtained pressures of 23 pounds per square inch in tests with samples of zinc powder containing 92 per cent. metallic zinc.

### Peculiarities Noted in Investigations

Most of the investigators call attention to the fact that water oxidises zinc dust at ordinary temperatures and liberates hydrogen. One report indicates that enough heat may be produced in the decomposition to ignite the hydrogen or near-by zinc dust. Manufacturers make a special effort to keep the powder dry, and, by a warning printed on the container label, some of them caution users against then danger of getting the material wet.

### Extent of the Hazard

An accurate idea of the extent of the explosion hazard in connection with the manufacture of aluminium, magnesium and zinc powder is difficult because many of the powder-producing plants are operated as a part of an establishment engaged in the manufacture of a number of metal products. The dust or powder may be considered a by-product at some plants, and the losses caused by explosions and fires in the powder-producing sections of metal plants have been listed separately in very few instances. From examination of the records, however, it is quite evident that small fires occur in such plants much more frequently than is generally supposed. Since any fire in the metallic dusts mentioned is the potential beginning of a serious explosion, and laboratory tests have demonstrated the ease with which these dusts can be ignited, it may be concluded that the explosion hazard

exists wherever aluminium, magnesium or zinc powder is manufactured or handled.

Increased use of both aluminium and magnesium powder has been noted during recent years, and the production of primary magnesium in 1939 was more than double the production in 1938. This increased production undoubtedly indicates greater use in cast parts, the machining of which creates a fire and explosion hazard.

### Explosion Prevention and Protection

In a plant where a spark or small fire may cause a serious explosion, fire prevention and fire protection are of the utmost importance; providing such protection, under conditions where the use of water and the common types of fire extinguishers serves only to intensify the fire, is a difficult problem. At present no satisfactory and safe method can be recommended for extinguishing a large fire in aluminium, magnesium or zinc powder. Water causes oxidation, and the release of hydrogen, hose streams or gas jets may throw dust into suspension and form explosive dust and air mixtures, and inert gas atmospheres that may retard ignition are ineffective in extinguishing fires that are well started. Violent explosions of magnesium powder have occurred in atmospheres in which the oxygen had been reduced to as low as 12%. The problem calls for research and experimentation and the development of a satisfactory method of combating the hazard. Small fires can be extinguished by using sand, talc or rock dust. Great care must be taken to avoid disturbing the burning powder when applying the sand or talc, and only men familiar with the explosion hazard should attempt to employ this method.

Protection becomes largely a question of fire prevention, although a few recommendations based upon the results of laboratory studies can be made. Thus: (1) Cleanliness is of the utmost importance, and dust should not be allowed to accumulate where it might be thrown into suspension in air and form an explosive mixture. (2) Powders should be kept dry to prevent heating and possible ignition. (3) All equipment should be grounded to prevent accumulation of charges of static electricity. (4) Precautions should be taken to prevent the formation of metallic or electric sparks. (5) All electric wiring and equipment should be of the type approved for use in atmospheres containing explosive metal dust, and remote control of electric circuits is desirable. (6) Magnetic separators should be used to remove tramp iron or other foreign material that might produce sparks in the mills or polishers. (7) Use of open flames and smoking should be prohibited. (8) Non-sparking tools should be used for repair work and for other activities as far as possible. (9) Heating should be by hot air only, with provision for heating the air with steam coils located outside the dust-producing section. (10) To reduce the hazard from fire and explosion it is recommended that the powder-making section of a plant be segregated from other parts or buildings and divided into small units. (11) Buildings used for powder-making should be only one storey, with a roof as light as practical and arranged to lift off readily in case of an explosion. (12) Buildings should be separated by not less than 50 feet of space with powder-making buildings at least 300 feet from occupied structures such as dwellings, stores or public buildings. (13) Dry sand, talc or other powders to be used to extinguish small dust fires should be stored in clearly marked or indicated containers at strategic points. (14) Fire companies that may respond to alarms from the metal powder-producing section should be warned against the use of water or extinguishers that may disturb the dust or intensify the fire.

Increased production and use of aluminium, magnesium, and zinc powder and scrap will make it imperative that an answer be found to the question: How can explosions of aluminium, magnesium and zinc powder be prevented, and how can fires in plants producing or handling these products be extinguished safely? Research is being planned to try to provide the answer.



## Copper-Nickel-Zirconium-Aluminium Alloys

*Data is given as a result of an investigation on the effect of zirconium and of zirconium-aluminium as hardeners on copper-nickel alloys having a one to one and a three to one ratio.*

**D**URING recent years copper-zirconium alloys have been shown to be subject to precipitation hardening, and a number of modified copper zirconium alloys have been described. Further data has been obtained by E. F. Nippes,\* who investigated the effect of zirconium and of zirconium and aluminium as hardeners on copper nickel alloys having a one-to-one and a three-to-one ratio. The two best alloys of aluminium-zirconium additions to those copper-nickel alloys were further investigated for possible industrial applications, the hardening agent being a compound of aluminium and zirconium containing about 70% of aluminium.

Copper-nickel-zirconium-aluminium alloys were first made by using a commercial copper-zirconium alloy as the source of zirconium. The composition of this alloy was 74.13% copper, 25.62% zirconium, 0.12% titanium and 0.13% iron. The alloys were prepared in a high-frequency furnace using alundum-lined crucibles. Electrolytic copper and nickel were melted down under a bottle glass slag, and after the melt had picked up sufficient superheat the glass slag was drawn and the melt deoxidised with silicon, desulphurised, and still further deoxidised by means of calcium. The copper-zirconium alloy was added piece by piece, the pieces being held under the surface of the bath by means of a nickel rod until solution occurred. Aluminium was then added, the bath deslagged, and the alloys cast into  $\frac{3}{4}$  in. round three-finger moulds. The recovery of zirconium as determined by analysis varied from 75 to 85%, while the aluminium recovery varied from 85 to 95%.

The alloys as cast were cold rolled to approximately  $\frac{1}{4}$  in. square rods and normalised for six hours at 1050° C. in a dry hydrogen atmosphere, after which they were water quenched to retain the solid solution. After polishing, etching and micro-examination they were aged at 500° and 600° in a coal gas atmosphere. A typical ageing series included 1, 2, 6, 12, 24 and 48 hours at the ageing temperature. The progress of ageing was followed by taking Vickers hardness numbers using a 10-kg. load, each value recorded being the average of at least three readings.

Twenty alloys were investigated in the first series and ten alloys in the second series, and the results obtained showed two alloys, one in each series, to give good results as regards increase in hardness upon ageing. In the first alloy containing 48.2% copper, 48.2% nickel, 1.18% zirconium and 2.35% aluminium, the hardness increased from 133 to 278 after 48 hours ageing at 600° C., while the second alloy containing 72.2% copper, 24.1% nickel 1.15% zirconium and 2.60% aluminium showed an increase from 118 to 274 after 10 hours ageing at 600° C. These two alloys, both of which were just within the solid solution curve at 1050° C., were selected for further investigation.

The two selected alloys were cold-rolled as cast from  $\frac{3}{4}$  in. round to approximately  $\frac{1}{4}$  in. square rod, heated for 6 hours at 1050° C. in a dry hydrogen atmosphere, and water quenched to retain the solid solution. After approximately 65% cold reduction (from  $\frac{3}{4}$  in. rod to 0.15 in. square rod) they were given a solid solution heat-treatment for 20 minutes. Further cold rolling and, finally, wire drawing gave a wire 0.091 in. in diameter, and these wires were given a solid solution heat-treatment at 1050° C. for 15 minutes. The effect of cold work on both alloys was then investigated by means of tensile, Vickers hardness,

and electrical resistivity tests, and showed the tensile strength and hardness to increase, the elongation to decrease, and the electrical resistivity to remain practically unaltered as the alloys were reduced by cold work.

Two sets of each alloy, one set in the form of wire 0.091 in. solid solution condition with no cold work, and the other in the form of wire 0.072 in. solid solution reduced 37.5% by wire drawing from 0.091 in. were aged at 500°, 550° and 600° C. in dry coal gas for 2, 4, 8 and 16 hours. As a result of tensile, hardness and electrical resistivity tests it was shown that in the solid solution, no cold work condition, the best results were obtained after 8 hours ageing at 600° C., when the tensile strength in the first alloy increased from 40.4 to 62.6 tons per sq. in. and the Vickers hardness from 136 to 279, and in the second alloy from 34.7 to 64.1 tons per sq. in. and 136 to 297 hardness. Both alloys showed a decrease in the electrical resistivity after ageing. In the solid solution, cold worked 37.5% reduction condition, the first alloy showed an increase in strength from 57.0 to 76.3 tons per sq. in., and in Vickers hardness an increase from 249 to 360 after ageing 8 hours at 550° C. The electrical resistivity decreased from 341 to 290 ohms. The tensile strength of the second alloy increased from 51.3 to 71.9 tons per sq. in., the Vickers hardness from 220 to 363, and the electrical resistivity decreased from 240 to 178 ohms after ageing for 4 hours at 550° C.

The effect of double ageing, that is, precipitation hardening followed by cold work and a second ageing period was investigated in both alloys. The first alloy, when in solid solution condition with no cold work, exhibited the best properties when aged 8 hours at 800° C as also did the second alloy. Both alloys in their aged condition were reduced 47% by wire drawing and re-aged for 2 hours and 4 hours in dry coal gas at 550° C. The effect of the double ageing as regards strength is shown in Table I.

TABLE I.

	1st Alloy	2nd Alloy
	Tons per sq. in.	Tons per sq. in.
Aged 8 hours at 600° C. ....	62.6	64.1
Aged 8 hours at 600° C., cold worked 47% .....	71.0	69.8
Aged 2 hours at 550° C. ....	87.3	75.5
Aged 8 hours at 600° C., cold worked 47%, re-aged 4 hours at 550° C. ....	85.6	81.1

TABLE II.

Condition	Tensile Strength Tons per sq. in.	Elong (2 in.) %
Solid solution of 1st Alloy, cold worked 37.5%, aged 8 hours at 550° C. ....	76.3	3.5
Solid solution of 1st Alloy, aged 8 hours at 600° C., cold worked 47% .....	71.6	5.0
Solid solution of 2nd Alloy, cold worked 37.5%, aged 4 hours at 550° C. ....	71.9	6.5
Solid solution of 2nd Alloy, aged 8 hours at 600° C., cold worked 47% .....	69.8	3.0

In general it was found that aluminium and zirconium were very effective as hardeners in alloys where the ratio of copper-nickel was one to one and three to one. The contours of the iso-hardness curves plotted from the first experiments on both series of alloys appeared to indicate that a compound of aluminium and zirconium containing 70% aluminium might be the cause of precipitation hardening. A summary of the best ageing conditions for the two alloys selected for further experimenting with corresponding properties are given in Table II.

Micro-examination of all the conditions in Table II. showed the second alloy to have a definite precipitated phase, whereas the first alloy showed slightly broader grain boundaries. The second alloy also showed complete recrystallization in the cold worked and aged condition, while the first alloy only showed partial re-crystallization. In both alloys better properties were obtained by cold work followed by ageing than by ageing followed by cold work. Double ageing gave better properties than single ageing.

\* *Metals and Alloys*, 1941, vol. 13, No. 3, pp. 294-300.



# Recent Research into Problems of Powder Metallurgy\*

By D. W. Rudroff, A.Am.I.E.E., M.Inst.F., F.R.S.A.

A review is made of recent laboratory research into certain theoretical and practical problems of powder metallurgy. Research of this kind is of particular importance in view of the existing gap between practical experience and theoretical knowledge in this important field. While the review refers in particular to the work of M. Y. Balshin, carried out in Russia, some comments specially contributed by Dr. E. A. Bánd, London, are also included.

## The Influence of the Pressing Conditions upon the $V_0$ versus $\log p$ Diagram

**Speed of Pressing.**—According to experimental data obtained by Balshin, a variation in pressing speed has but little influence upon the magnitude of the pressing modulus  $L$ , and upon the density of the pressed piece. Theoretically, the pressing modulus  $L$  should somewhat increase with the speed of the pressing, while the density should show a decrease. This conclusion is drawn from the fact that the re-disposition of the particles and their plastic deformation requires a certain length of time. But there are other considerations which lead to the same conclusions.

In the pressing process, pressure energy is absorbed by the friction prevailing between the particles as well as between the particles and the mould. Energy is likewise absorbed in the process of deformation. Considering a stratum located at a certain distance from the pressure exerting plunger, it is quite obvious that with a high pressing speed, this stratum will exact upon the underlying stratum a pressure  $\Delta p$  which is smaller than  $p$ . But if pressing takes place slowly, sufficient time will be available for a gradual equalisation of pressure, that is to say, the stratum pressure will finally rise from  $\Delta p$  to  $p$ . As Balshin notes, this phenomenon was first referred to by V. S. Rakovskii† in connection with his investigations of pressing characteristics.

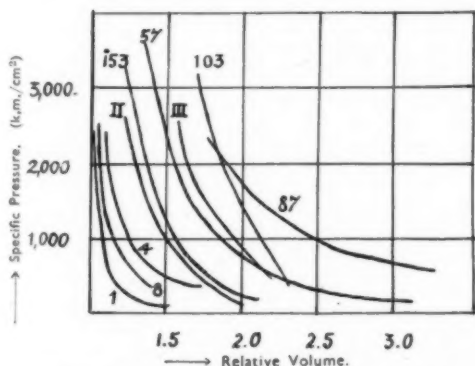


Fig. 6.—Pressing curves obtained with a Gagarina press.

1. Pulverised lead, when loosely heaped, 3.98 grms./cm.<sup>3</sup>
4. Electrolytic silicon, when loosely heaped, 1.10 grms./cm.<sup>3</sup>
8. Pulverised silicon, when loosely heaped, 3.5 grms./cm.<sup>3</sup>
133. Electrolytic iron, when loosely heaped, 2.7 grms./cm.<sup>3</sup>
- III. Electrolytic copper, when loosely heaped, 0.97 grms./cm.<sup>3</sup>
103. Tungsten, when loosely heaped, 4.18 grms./cm.<sup>3</sup>
- II. Copper (Brand M oz.), when loosely heaped, 3.51 grms./cm.<sup>3</sup>
87. Iron, when loosely heaped, 0.57 grms./cm.<sup>3</sup>

As exemplified by the diagram reproduced in Fig. 7, the theoretical relationship between speed of pressing and modulus of pressing, and also of the density, can be actually verified by test. There are, however, cases in which the density of the pressed piece can actually increase with the speed of compression. This phenomenon is particularly noticeable in the case of mixed powders. In the opinion of Balshin, this phenomenon may be explained by some kind of liquefaction process which makes its

appearance in the pressing process, which liquefaction may be due to differences in the plasticity and mobility of the components of the powder mixture. Irregularities in local distribution and structural differences as well as differences in the chemical composition of the components of the mixture may likewise play their part. This liquefaction process becomes more pronounced with decreased speed of pressing, and it may well lead to a decrease in density caused by a disintegration of the mixture into its components. But in multi-layer pressings this decrease in density may also be caused by residual elasticity, as such pressings show a smaller stability because of their heterogeneous composition. But it may be added that A. Rostarchuk‡ has shown that the infiltration of the air increases with decreasing speed of pressing, which may also cause a fall in the density of multi-layer pressings. Thus, in a number of cases, lower speed of pressing gives less good results.

**The Influence of the Height of the Pressed Piece.**—In his investigation of the influence of the height of the pressed piece on the characteristics of the pressing process, Balshin proceeds from the formula.  $h_k = h/D_0$ , where  $h_k$  is the height of the piece compact state,  $h$  is the height actually reached by pressing, and  $D_0$  is the relative density expressing the ratio between the density actually obtained by compressing and the ideal density in the state of compactness. This relative density is found to be dependent upon several factors.

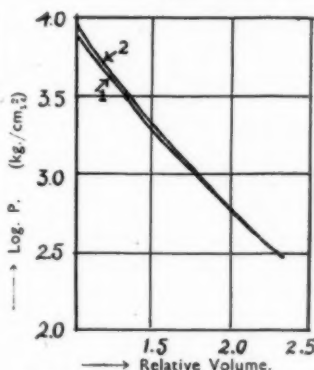


Fig. 7. Electrolytic Copper.

1. Compression speed 2 mm./min.
2. Compression speed 4 mm./min.

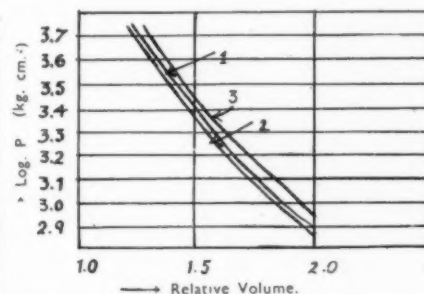


Fig. 8.—Electrolytic copper, when loosely heaped, 1.42 grms./cm.<sup>3</sup>.

Height in Compact State:

1.  $h_k = 0.6$  mm.
2.  $h_k = 4.0$  mm.
3.  $h_k = 8.0$  mm.

It is clear that with increasing value of  $h_k$ , the speed of deformation of the pressed piece increases, if the speed of descent of the plunger is kept constant irrespective of the varying height  $h_k$ . It is  $c' = c/h_k$ , where  $c'$  is the relative speed of deformation, and  $c$  is the absolute speed of pressing. But it must not be overlooked that the pressure losses in the powder layers increase with increasing value of  $h_k$ . This fact increases the modulus of pressing as well as the pressure required for compression of the piece. Owing to these factors, the maximum density obtainable is usually obtained with  $h_k = 1$  to 2 mm. As shown in Fig. 9 (and also evidenced by the graph given in Fig. 8), there definitely exists an optimum value for  $h_k$  which

\* Continued from page 178, April, 1941, issue.

† loc. cit.

‡ A. Rostarchuk. *Amerikanskaya Promishlennost i Tekhnika*. No. 4 and 5, 1937.

renders a maximum density. Both smaller and larger heights lead to a decrease in density. This fact is particularly well illustrated by the graph reproduced in Fig. 9.

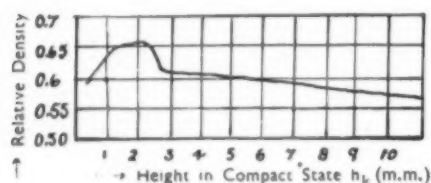


Fig. 9.—Pressed tungsten pieces, density versus height in compact state. ( $p$  = constant.)

This phenomenon of diminished density with heights other than the optimum height can be explained by the following factors:

1. The residual elasticity of the pressed piece becomes particularly pronounced in pieces of small height. This is due to the fact that in such pieces the mutual friction between the particles is not large enough to cause sufficient braking effect upon the forces of residual elasticity. In order to illustrate this point, Balshin refers to the fact that in a piece with a height  $h_k = 1$  mm. this height is made up by only 25 particles, if the particle size amounts to 40 microns.

2. In the case of greater height, the planes of equal pressure are curved, while in the case of small height, they are flat. Such curvature exerts a braking effect upon the residual elasticity. Maximum density usually lies on the side of comparatively great height, high pressing speed and coarse powders. The fact that the density decreases with diminished height of the pressed piece, limits the production of pressed pieces to a minimum height of ca. 1 mm. It should also be noted that the height of the pressed piece is of considerable influence upon the variation in pressure encountered for a given density. But the modulus of pressing changes but very little, this fact being evidenced by the curves shown in Fig. 8. As Balshin states, the phenomenon of liquefaction becomes more pronounced with increasing height of the piece, if identical absolute pressing speeds are employed. It therefore follows that with increased height of the pressed piece, it is sometimes advantageous to increase the speed of the press.

*The Influence of the Cross-Sectional Area of the Pressed Piece upon the Characteristics of the Pressing Process.*—If the diameter of the press mould is increased, two factors appear in the process of pressing which oppose each other. On the one hand the specific influence of friction between the powder and the walls of the mould falls with increasing mould diameter, provided the pressure is kept constant. This fall in friction is in straight line relationship with the diameter of the mould. Therefore it can be said that the pressure requirements diminish with increasing diameter of the mould. On the other hand, however, the speed of lateral deformation of the powder increases in direct proportion with the diameter of the mould. (This is due to the fact that the amount of powder contained in the mould increases with the square of the diameter, while the side wall surface increases in direct proportion with the diameter.) In certain cases, this phenomenon can become noticeable by an increase in the magnitude of the pressing modulus and a fall in the density of the pressed piece. This fact is illustrated by the chart reproduced in Fig. 10. It is therefore recommended that the pressing speed should be decreased with increasing diameter of the mould. But it is emphasised that these statements should be treated with reserve, as the number of tests made was not quite sufficient to prove beyond all doubt that it is not the influence of the condition of the walls of the mould (varying degree of wall roughness) which is responsible for the influences at present ascribed to the

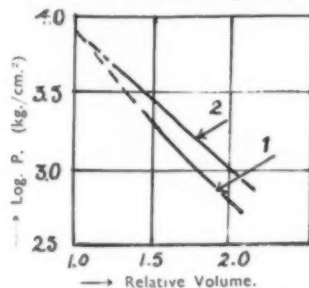


Fig. 10.—Electrolytic copper when loosely heaped, 1.5 grms./cm.<sup>3</sup>.  
1. Diameter of mould, 15 mm.  
2. Diameter of mould, 10 mm.



Fig. 11.

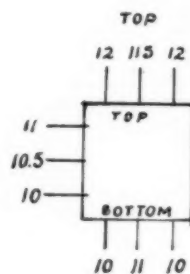


Fig. 12.

*The Influence of Lubricants Employed for Decreasing the wear of the mould.*—Liquid additions such as glycerine, benzine, oil, water, etc., considerably decrease friction, and thus the wear of the mould, without, however, having much influence upon the pressing diagram. As Balshin explains, this is due to the fact that the fall in electric potential under the influence of the increase in the dielectric constant is compensated for by the decrease effected in the contact distances. Thus, the cohesive forces do not change in magnitude. On the other hand the application of high pressure tends to squeeze the liquid out of the powder. It may be mentioned that a considerable fall in pressure requirements was observed by Hardie, who succeeded in pressing pieces of greatly increased depth by means of the wet process.

*The Influence of the Application of Double-sided Pressing upon the pressing characteristics.*—Double-sided pressing yields substantially identical characteristics as compared to one-sided pressing, although some decrease in the pressing modulus obtains. As Fig. 13 shows, the influence of double-sided pressing upon the density distribution in the pressed piece, is, however, considerable.

### The Distribution of Density in Multi-Layer Pressings

The distribution of density in a multi-layer pressing (Fig. 11) is quite uneven. In view of the curved layer boundaries observed in the piece, it is quite easy to predict that the density will be greatest at the top in the vicinity of the edges, while at the bottom of the piece, maximum density will be found near the centre. This conclusion is fully confirmed by test results such as shown in Fig. 12. This test refers to the distribution of hardness (measured in Shore hardness) in a pressed cube of copper powder.

For the interconnection between fall in density and distance from the upper surface of the piece, Balshin gives the following mathematical relationship. It is:

$$(13) -dp = a \cdot p \cdot dh,$$

where  $a$  is the proportionality constant. By integration it is found that the decrease in pressure with the depth  $h$  is expressed by  $\ln p/p_h = a \cdot h$ , or (15)  $\log p/p_h = A \cdot h$ , where  $p$  is the pressure at the top surface of the piece and  $p_h$  that prevailing at the distance or depth  $h$ .  $A$  is a constant. According to equation (7a), it is

$$\log p/p_h = -L (V_0 - V_{0h}) = L \cdot \Delta V_0, \text{ or } (16) \Delta V_0 = (A/L) \cdot h,$$

that is to say, the decrease in relative volume with the depth is in proportion with the depth. Within a sufficiently small range of density variations,  $\Delta V_0$  can be considered to be in proportion with  $-\Delta D_0$ . Therefore, it is:

$$-\Delta D_0 = (B/L) h \quad (17) \text{ and}$$

$$-\Delta d = (C/L) h \quad (18),$$

where  $-\Delta D_0$  and  $-\Delta d$  represent the decrease in relative density and density, respectively,  $B$  and  $C$  are proportionality constants and  $L$  represents the pressing modulus.

This shows that the decrease in density takes place in approximately linear relationship with the depth. But this does not apply to the bottom part of the pressed piece where (according to V. S. Rakovsky\*) the influence of the immovable press bed may sometimes lead to the

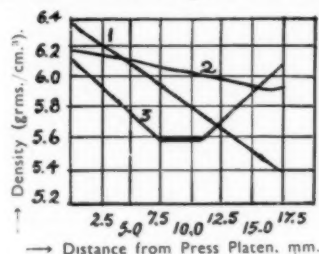


Fig. 13.

1. Electrolytic copper, when loosely heaped, 1.42 grms./cm.<sup>3</sup> without graphite, one-sided pressing.
2. Electrolytic copper, with 4% graphite.
3. Electrolytic copper, without graphite, double-sided pressing.

creation of a higher density. The fall in density with the depth as observed by Balshin is charted in the diagram reproduced in Fig. 13. Balshin summarises his findings regarding the various factors which influence the density variation with the depth as follows:

1. The fall in density with the depth increases with decreasing diameter of the mould.
2. The fall in density with the depth is usually less pronounced in the case of hard and coarse powders. And this applies also to powders possessing a large pressing modulus.
3. Double-sided pressing considerably improves the density distribution.
4. Inclusion of graphite strata considerably lowers the fall in density; 4% of graphite diminishes the fall in density approximately five to six times. Additions of glycerine, etc. have a similar effect.

#### Other Formulations of the Relationship Between Pressure and Degree of Compression as Proposed by Balshin

Owing to the fact that the equation (7) is based on a constant pressing modulus  $L$ , this equation will hold true only under ideal conditions. In order to make this equation conform with actual conditions, allowance must be made for the fact that in actuality,  $L$  varies with regard to pressure or degree of compression. It is, however, not possible to establish a mathematical formulation of this relationship. With this point in view, Balshin has studied two other methods of formulation, which might possibly take the place of equation (7).

The first of these is based on expressing the coefficient  $l$  (contained in equation (3a)) by

$$l = m/V_0, \text{ where } m \text{ is a constant.}$$

It is therefore

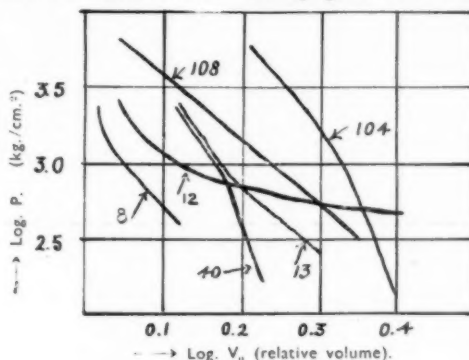
$$\frac{dp}{p} = -m \frac{dV_0}{V_0}. \text{ By integration it follows that } p V_0^m = \text{constant. (20)}$$

This relationship may be said to be analogous to Boyle-Mariotte's law for gases, excepting that  $m \neq 1$ .

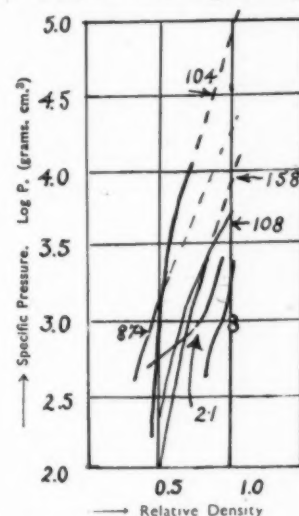
Balshin has found that in the majority of powders investigated by him, the factor  $m$  varied between 4 to 10, while variations in a range between 1 to 30 also occurred. Referring to the graph reproduced in Fig. 14, it is clearly seen that indeed  $m \neq \text{constant}$ . The other formulation investigated by Balshin is based on the assumption that

$l = n/V_0^2$ , where  $n$  is a constant. This leads to the expression  $\frac{dp}{p} = -n \frac{(dV_0/V_0^2)}{V_0^2} = n \cdot d \cdot D_0$ , where  $D_0$  is the relative density of the pressed piece. By integrating and introducing Brigg's logarithm, it is  $\log p/p' = N (D_0 - D_0')$  (21) where  $N = 0.434 n = \text{constant}$ .

However, the graph shown in Fig. 15 for the relationship between  $D_0$  and  $\log p$  clearly shows that  $N \neq \text{constant}$ . Regarding the accuracy obtainable with the various formulæ investigated, Balshin states that equation (7) usually gives somewhat low values in the range of high

Fig. 14.—Log  $p$  versus  $\log V_0$ .

12. Electrolytic silicon, when loosely heaped, 1.10 grms./cm.<sup>3</sup>
8. Pulverised silicon, when loosely heaped, 3.5 grms./cm.<sup>3</sup>
40. Copper, spherical particles, when loosely heaped, 4.5 grms./cm.<sup>3</sup>
13. Copper, grinding dust, normalised at 200°C., when loosely heaped, 1.16 grms./cm.<sup>3</sup>
108. Electrolytic copper, when loosely heaped, 1.42 grms./cm.<sup>3</sup>
104. Tungsten, when loosely heaped, 4.18 grms./cm.<sup>3</sup>

Fig. 15.—Log  $p$  versus  $D_0$ .

8. Pulverised silicon, when loosely heaped, 3.5 grms./cm.<sup>3</sup>
21. Electrolytic silicon, when loosely heaped, 1.1 grms./cm.<sup>3</sup>
104. Tungsten, when loosely heaped, 4.18 grms./cm.<sup>3</sup>
87. Mild Iron, when loosely heaped, 0.37 grms./cm.<sup>3</sup>
108. Electrolytic copper, when loosely heaped, 1.42 grms./cm.<sup>3</sup>
158. Iron, when loosely heaped, 2.70 grms./cm.<sup>3</sup>

pressures, while equations (20) and (21) give high values. The relative usefulness of the three formulæ is said to vary according to the kind of powder investigated, but in general, equation (7) will give satisfactory results.

Referring back to Balshin's statement that small particles are more apt to fill up existing voids and would thus display fluid-like behaviour, Dr. Bánó points out that this matter has recently been mentioned by W. D. Jones,\* in his notes on the extrusion of metal powders. The latter states that powders, particularly fine-grained powders, behave in many respects like liquids. Only recently, R. Selig\*\* has made a similar remark. Both workers, however, have only briefly touched upon this subject, and it would appear indeed an interesting task to study how far a powder may be considered as a "liquid solid."

It is to be hoped that the research undertaken by Balshin will also lead to an investigation of the conditions which prevail when mixtures of powders of sharply divergent particle size and pronounced difference in hardness are pressed together.

In Dr. Bánó's opinion this matter is of great practical and theoretical interest. Certain powder metallurgical products in which hard and large particles are surrounded by, or embedded in, particles much softer and smaller than themselves, are manufactured by means of an extrusion process; and if it were possible to survey, completely or approximately, what happens during the extrusion process, particularly as regard homogeneity and density of the final product, useful conclusions would doubtless be arrived at. Moreover, in the aforementioned case, the shrinkage incurred during the heat-treatment will not be of primary importance as the bodies compressed by the extrusion process have already undergone a very high degree of reduction. But it should be borne in mind that there is also a certain group of metal-ceramic products which comprise a combination of hard and softer powder. In this respect, particular interest attaches to a number of British and foreign patent specifications concerning the production of metal-bonded diamonds and other abrasives in connection with the manufacture of grinding and lapping wheels, and similar products. In their manu-

\* W. D. Jones: "Extrusion of Metal Powders," *Met. Ind.* (London).

\*\* R. P. Selig: "The Pressing of Metal Powders, 1940, 57 (2), p. 27, *Met. and All.*, Vol 12, No. 8, 1940.

\* loc. cit.



facture, powder metallurgical methods are employed, and the problem of shrinkage of such pressed compacts when exposed to elevated temperatures will become important. Shrinkage during heat-treatment will obviously obey other laws than in the case of mixtures of practically homogeneous powders. Much information will, of course, be gained from practical experience. But, no doubt, if it would become possible to foretell shrinkage and final porosity, etc., with a reasonable degree of accuracy, the design and process requirements (such as pressure requirements) would benefit greatly from such knowledge.

An approach to such problems from the mathematical angle appears also quite promising. The density of the

matrix in the neighbourhood of the coarse and hard particles will be different from the density at greater distance from the particles. Within the pressed compact, hard bodies will act as centres of disturbance affecting the uniform pressure propagation. If it is assumed that fine powders actually have a certain ability to flow and to behave like fluids, it may also be assumed that a vortex-like pressure distribution will occur in the vicinity of the coarse particles, that is to say, around the centres of disturbance. There might even be a possibility that Prandtl's theory dealing with the flow of fluids and with the phenomena arising from flow obstructions could be applied to problems of powder metallurgy.

## Developments in Metal Spraying Technique

*The latest achievement in this field is the development of the electric pistol in which two wires are fed and caused to form an arc when electricity is passed through them. Metal spraying is being successfully applied to the making of dies used in the pressing of plastic materials.*

**T**HE process of building up metal coverings by means of spraying was given considerable impetus about thirty years ago, when Dr. M. U. Schoop, of Switzerland, developed a metal spraying pistol which could be moved freely over the surface to be sprayed, and consequently could reach without difficulty all parts of the object required to be covered with metal. By this method the metal to be sprayed is fed to the pistol in the form of wire where it is melted and atomised.

Fuel gas and oxygen at a pressure of about 20 lbs. per sq. in. supply the heat for melting the wire, and air at 35 to 60 lbs. per sq. in. is used to atomise the melted metal. The two compressed gases are introduced ready mixed. Many modifications of this type of pistol have been introduced, frequently incorporating improvements for spraying with specific metals. Thus, a modified design was specially designed for coating metals with lead or tin, using compressed air, nitrogen or carbon dioxide, heated up to 450° C., instead of by a compressed gas flame. The heating of the atomising gas is effected by making it pass, before leaving the nozzle, through a long spiral-shaped coil of fine tubing, which is heated externally by two oxy-acetylene burners.

Another type of pistol recently introduced by Metallisation Ltd. follows the general construction of gas-fed pistols, and consists of three main members, of which the most important is the nozzle. The nozzle consists of a nichrome tipped, slightly conical, inner tube through which the wire is fed. This tube carries round its external surface grooves which, when covered by a cap, serve to convey an almost explosive mixture of a fuel gas and oxygen under pressure. The ignition of this mixture forms a blowpipe flame into the centre of which passes the wire, which melts in the hot zone, but round the gas nozzle is placed another cap, so that between them compressed air can be passed to the jet which atomises the melting wire and causes it to be sprayed where directed.

The wire is fed through the nozzle by means of rollers driven by a train of gears actuated by a compressed air turbine contained in the tool. The feed of the gases and air to the jet and the air to the turbine is controlled by a composite valve with one control. The fuel gases used in this country are generally coal gas or propane. The refinements of this metal spraying pistol include an extra large turbine, a wire-tensioning device, an external control of wire rollers, and a special type of valve.

What is regarded as the latest achievement in this field is the development of the electric pistol at the M. U. Schoop Metallising Works. In this new type two wires are fed to the tool; at the nozzle outlet these wires are brought into contact with each other so that a melting arc is caused to

form between them as soon as electric current passes through. The ends of the wires are first melted and then atomised by compressed air and driven through the nozzle. The principle of the feed mechanism is the same as the types already described, excepting that the feed and pressure rollers are duplicated to accommodate two wires and the wire guides are insulated from each other. The apparatus can be used either for direct current or for alternating current, but experience has shown direct current to be preferable. If no direct current is available it is found profitable to use converters.

### Applications

The applications of the metal spraying process are practically unlimited; they are so well known that only brief reference to some of the principal applications need be made here. Thus, for instance, the provision of a firmly adhesive metal coating as a protection against corrosion; the repair of engine and cylinder heads which have developed cracks; the building up of working parts which have been subjected to wear; the manufacture of metal surfaced wood; the application of metallic designs to textiles; the repair of casting defects, etc.

More recently the process has been applied successfully in the production of metal dies for plastic substances, by which substantial economies can be effected. Pressed articles formed from plastic substances, such as bakelite, have been applied to an ever increasing extent in recent years; they are produced by pressing the plastic substances into a metal die. The plastic substance is introduced in the form of powder, tablets or chips. In the simplest case the required die consists of the stationary external mould and the inner removable part—the plunger. The construction of such dies is generally a complicated and costly matter. Considerable experience is necessary to shape and produce the dies so that the pressed parts conform to the desired shape and size when produced from them.

By means of the metal spraying process the construction of these dies is fundamentally changed and the difficulties associated with their production is substantially reduced. A plaster of paris pattern, which reproduces the object to be formed of plastics, is kept under the spraying pistol until all parts are sufficiently covered with metal. Subsequently the plaster pattern is removed and the metallic die left can be used in the press. The die is a faithful reproduction of the pattern and is done with such precision that no finishing with chisel or file is necessary. In addition to plastic, like bakelite, steel dies made in this way are suitable for making shaped articles in rubber.

# A Study of Some of the Factors Affecting the Resistance of Cast Iron to Deflection Under Load at High Temperatures

By L. W. Bolton, A.M.I.Mech.E.

British Cast Iron Research Association

*Many factors influence the resistance to deflection of cast iron at elevated temperatures and the effect of composition, structure and casting conditions on this phenomenon have been studied, a report of which is given in this paper.\* The report also includes the results of an examination of the rigidity of two types of austenitic cast iron, which were found to have good resistance to deflection at the temperature of the tests.*

ABRIDGED.

ORDINARY grey cast iron fails at high temperature through growth and scaling, but special irons have been developed in recent years which possess resistance to a marked extent to both these effects. The extended application of these irons in industry has made it desirable to have some information regarding their resistance to deformation under prolonged application of light loads at high temperatures.

The work described in this report was carried out with a view to supplying some of this information, and since the results of quantitative creep tests at high temperatures are extremely difficult to interpret for purposes of design, it was felt that the work should not be confined to actual creep tests on the special irons, but rather should be designed with a view to studying the influence of composition, structure and casting conditions on this phenomenon. In this way it was hoped to obtain data on the relative resistance to deformation under load at high temperatures of various types of heat-resisting cast irons which are now available.

Most heat-resisting cast irons have a fine graphite structure, and some owe their qualities to the presence of an abnormally high silicon content (*i.e.*, more than 4.5%). Others are austenitic, and consequently are far less rigid at room temperature than pearlitic or ferritic irons. It is sometimes desirable that the irons contain a moderate quantity of phosphorus in order to improve the castability of the metal. For these reasons, special attention has been given in this work to the influence of graphite size, variations in silicon and phosphorus contents, and to alloying employed to the extent of rendering the structure of the iron austenitic. Some data on carbon steels of varying carbon content have also been obtained.

For the purpose of this exploratory work, a method of testing has been developed which consists essentially of transverse loading a bar of standard dimensions at one end, while the other end is rigidly held, the stressed portion of the bar being held at a pre-determined constant temperature. Details of the apparatus used and the method of carrying out the test are described below.

After consideration of the various industrial applications in which cast iron is used at high temperatures, it was decided that information was most needed on its resistance to deformation at between 800° C. and 900° C. A temperature of 850° C. was therefore chosen for the investigation.

## Apparatus Used and Method Employed in the Test

The layout of the apparatus used is shown in Fig. 1. The specimen (D) is a bar 7 in. long and 0.6 in. in dia., reduced to 0.5 in. in dia. for a distance of 1 in. near one end, for the purpose of localising the stress. One end of the bar is rigidly held in a heavy heat-resisting nickel-chromium-alloy holder (B), clamped to the base of the apparatus by means of stout cast iron brackets. The test-piece is loaded at the free end with weights (E), and a

system of levers (F) amplifies the movement of the pointer at the end in the ratio of 10 to 1, this movement (*i.e.*, deflection at the free end) being recorded on a moving drum (G). In order to eliminate the effects of vibration, the whole apparatus is suspended on springs (H). The test-piece is raised to, and maintained at, the required temperature by means of a resistance furnace (A), well lagged with kieselguhr. On account of the massive size of the holder (B) the rest of the apparatus was also thoroughly insulated with kieselguhr and slag wool (C). The temperature of the specimen was obtained by means of a platinum/platinum-10% rhodium thermocouple the hot junction of which could be moved along the bar for a distance of 1 in. The furnace temperature was not thermostatically controlled, but the variations in temperature did not exceed  $\pm 7^\circ \text{C.}$ , and these variations were found to be without effect on the manner in which the bars deflected under load.

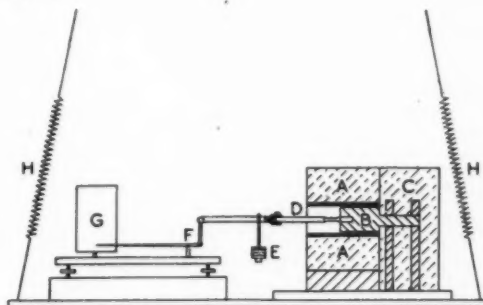


Fig. 1.—Apparatus for examining the rigidity of cast iron at elevated temperatures.

In carrying out the test, the furnace was slowly raised to the required temperature, and a steady temperature state was reached in approximately five hours from the time of switching on the furnace. During this heating-up period, the test bar was supported at the free end to prevent any sagging under its own weight. The weights used at the free end were such that the transverse stress at the narrowed part of the bar near the fixed end could be increased in steps of 0.1 ton per sq. in. from 0 to 2 tons per sq. in.

The effect of applying a load at the free end of the bar was to cause a fairly rapid rate of deflection for the first three or four hours, but after this the rate of deflection gradually decreased and then remained constant. At the end of a 24-hour period, the load was stepped up by an increment of 0.1 ton per sq. in., which was maintained for another 24 hours, and this process was repeated until the bar had bent through an angle of approximately 10°. It is worthy of note that even the most brittle of cast irons such as the high-silicon and high-phosphorus irons, were found to deform to this extent at 850° C. without breaking.

The tests carried out showed that the section of the bar as-cast had a considerable influence on the manner in

\* Iron and Steel Institute, 1941, Autumn General Meeting (advance copy).

which the test-piece was deformed under load at high temperatures. It was found, for instance, that test-pieces machined from thick cast sections were less rigid than those machined from thin sections of the same iron, and, in interpreting the results, this factor has to be taken into consideration.

### The Influence of Silicon on the Rigidity of Cast Iron at 850° C.

The ordinary common grey iron of medium silicon content, often used at high temperatures, usually fails ultimately from scaling and growth. Norbury and Morgan<sup>1</sup> have shown that if the graphite can be kept in a fine state of division, high-silicon cast irons have resistance to scaling and also a marked resistance to failure from growth. Such irons, having a silicon content of approximately 5%, together with a fine graphite structure, are known as Silal. The influence of additions of silicon to cast iron is well known, the matrix becoming harder and more brittle with increasing silicon. The eutectic carbon content is reduced and the high-silicon cast irons with a silicon content of 14% to 16%, used at present mainly for their resistance to chemical attack, contain usually less than 1.0% of total carbon, even when melted in contact with carbon i.e., in the cupola.

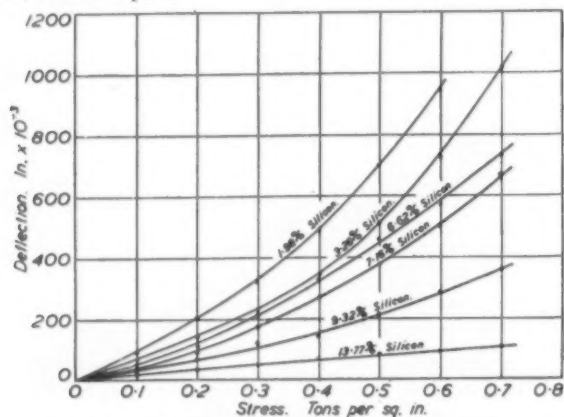


Fig. 2.—Deflection of Series A bars at 850° C.

A series (A) of bars with increasing silicon contents, ranging from 2% to 14%, was tested, the actual compositions being given in Table I, and the results of the tests are plotted in Fig. 2. The cast size of the bars was 0.65 in. in dia.

TABLE I.  
COMPOSITIONS OF IRONS, SERIES A (INCREASING SILICON CONTENTS).

No.	T.C.	Si.	Mn.	S.	P.
1	3.10	1.98	1.16	0.031	0.022
2	3.33	3.28	0.75	0.019	0.067
3	2.15	6.62	1.19	0.028	0.034
4	2.67	7.16	1.17	0.031	0.031
5	1.63	9.32	1.19	0.011	0.100
6	1.07	13.77	1.09	0.014	0.125

It will be seen from the curves in Fig. 2 that silicon exerts a stiffening influence on cast iron at the temperature of the tests. The iron containing 6.62% of silicon is of the Silal type and contains graphite in a finely divided state. The graphite flakes in the 13.77% silicon iron are also small, but those in the other two high-silicon irons are relatively coarse. Fig. 3 shows deflections plotted against silicon contents at a load of 0.5 ton per sq. in., i.e., total deflection at the end of the fifth day of the test in each case. This shows clearly the increase in the rigidity of the irons as the silicon content is increased.

Air was able to enter the furnace during the tests, and this led to some scaling and growth, especially in the case of the low-silicon irons. Wastage of the specimens through scaling may be a contributory cause of the lack of rigidity of the two low-silicon irons. It will be noted from Fig. 2 that the deflection of the iron containing 3.28% of silicon was only slightly greater in the early stages of the test

than that of the specimen which contained 6.62% of silicon. The sudden falling-off in the rigidity in the case of the lower-silicon bar as the test proceeded and as the load increased may be explained partly by this deterioration of the metal under heat. The scaling of the Silal bar was only superficial, as was also that of the other high-silicon irons. An interesting point is that these high-silicon irons, which, as already mentioned, are extremely brittle in the cold, were found to bend under prolonged stress at 850° C. The bar containing 13.77% of silicon gave a permanent deflection of 0.86 in. at the free end of the test-piece under a stress of 1.7 tons per sq. in. after twelve days at this temperature. (The stress was increased at the rate of 0.2 tons per sq. in. every 24 hours after 0.7 tons per sq. in. had been reached.)

The results of these tests show that additions of silicon of the order of 7% and more considerably increase the resistance of cast iron to deformation under load at high temperatures.

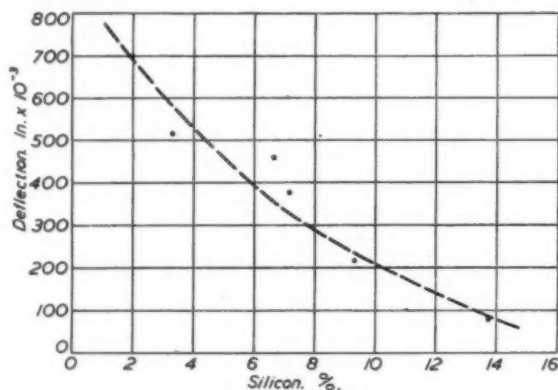


Fig. 3.—Deflection of Series A bars after five days with total stress of 0.5 tons per sq. in. at 850° C.

### The Influence of Phosphorus on the Rigidity of Cast Iron at 850° C.

In examining the influence of phosphorus, a base cast iron containing 5.5% of silicon was used, as this material scaled only slightly and had a very small growth. In this series (B) of bars tested, the phosphorus content varied between 0.4% and 1.1%. The as-cast size of the bars was 0.875 in. in dia.

The analyses of the bars used are given in Table II.

TABLE II.  
COMPOSITIONS OF IRONS, SERIES B (INCREASING PHOSPHORUS CONTENTS).

No.	T.C.	Si.	Mn.	S.	P.
7	2.40	5.59	1.20	0.035	0.377
8	2.47	5.50	1.17	0.043	0.639
9	2.42	5.42	1.14	0.039	0.927
10	2.41	5.42	1.13	0.040	1.100

Fig. 4 shows the deflections of these irons under stress at 850° C. It will be seen that additions of phosphorus progressively increase the stiffness of the metal at high temperatures. This stiffening influence is clearly shown in Fig. 5, where deflections are plotted against phosphorus contents for a stress of 0.7 tons per sq. in., i.e., total deflection of the specimen at the end of the seventh day of the test in each case. With the exception of the phosphorus content, the analyses of the bars are very similar, and the microstructures were very much alike. All the bars scaled only superficially, so that it would appear that the differences in rigidity are entirely due to the differences in phosphorus content. It should be noted, however, that the graphite size of the specimen containing 1.100% of phosphorus, the most rigid under test, was slightly coarser than that of the other bars in this series.

In order to examine the influence of phosphorus on cast iron of lower silicon content than Series B, two ordinary grey-iron bars (Nos. 11A and 12A) containing approximately 3.2% silicon, but with widely differing phosphorus contents, were tested (Series C). The as-cast size of the

<sup>1</sup> A. L. Norbury and E. Morgan, *Journal of the Iron and Steel Institute*, 1931, No. 1, p. 413.



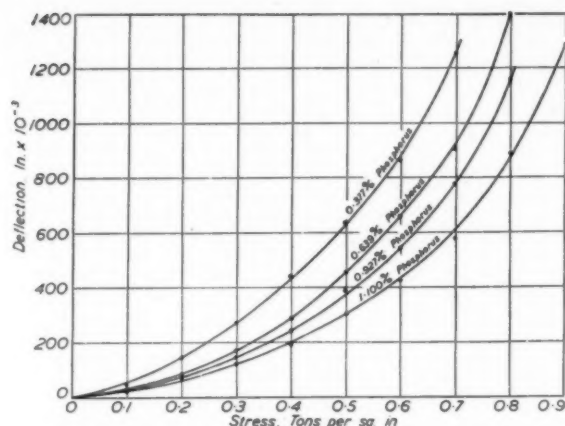


Fig. 4.—Deflection of Series B bars at 850° C.

bars was 0.65 in. in dia. They were produced under similar conditions to the bars in Series A, and an addition of ferro-phosphorus (20% phosphorus) was made in the case of bar 12A.

The analyses are shown in Table III., and the results obtained are plotted in Fig. 6 (two lower curves).

TABLE III.

COMPOSITIONS OF IRONS, SERIES D (SMALL- AND LARGE-DIAMETER BARS).							
No.	Cast Diameter	In.	T.C.	Si.	Mn.	S.	P.
11A*	0.65	..	3.33	..	3.28	..	0.019
11B	1.75	..	..	..	..	..	0.067
12A*	0.65	..	3.18	..	3.18	..	0.040
12B	1.75	..	..	..	..	..	1.320
13A	0.65	..	2.53	..	5.75	..	1.06
13B	1.20	..	..	..	..	..	0.048
14A	0.65	..	2.67	..	7.16	..	1.17
14B	1.20	..	..	..	..	..	0.031

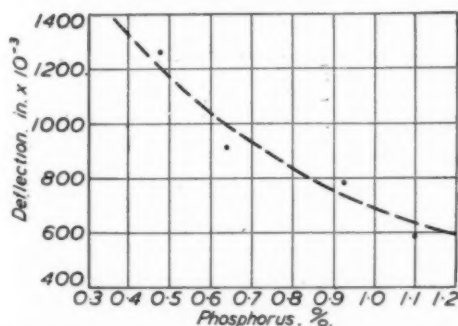
\* Bars 11A and 12A constitute also Series C, high and low phosphorus contents.

It will be seen that the higher-phosphorus bar is more rigid than the one with low phosphorus, although the difference in rigidity in this case is less marked than would be expected from the results obtained in Series B. Both bars in Series C, however, scaled on the surface and suffered from growth, and it is likely that this to some extent masked the influence of the differences in phosphorus content. The tests on bars of Series B and C do, however, show that additions of phosphorus increase the resistance of cast iron to deflection at 850° C. over the range of silicon contents of the metal, 3.18-5.75%.

#### The Influence of Graphite Size on the Rigidity of Cast Iron at 850° C.

In order to examine the influence of graphite size, bars were cast in two different sizes from four different compositions. In each case the bar cast to the larger original

Fig. 5.—Deflection of Series B bars after seven days with total stress of 0.7 tons per sq. in. at 850° C.



diameter contained graphite in larger flakes than the small-cast-diameter bar. The actual analyses of these bars are given in Table III.

Specimens for testing at 850° C. were turned from these

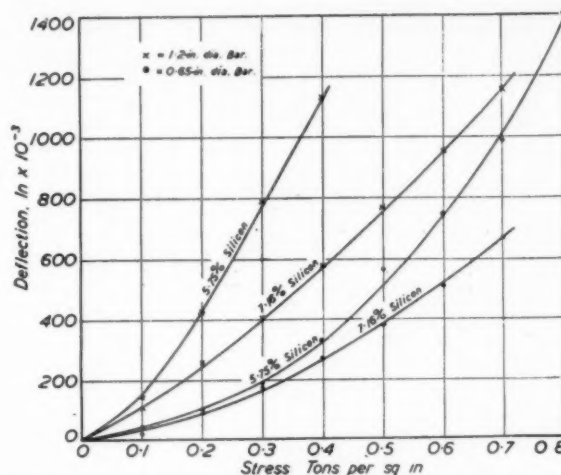


Fig. 7.—Deflection of bars of differing silicon contents, Series D, at 850° C.

bars. The results obtained on bars 11A and 11B and 12A and 12B are plotted in Fig. 6. These bars have similar carbon and silicon contents, but contain different amounts of phosphorus. It will be seen that the smaller-cast bars resist deflection at 850° C. better than the larger bars of the same composition in each case. The large-cast-diameter high-phosphorus bar is more rigid than the large-diameter low-phosphorus bar, showing that the phosphorus has a stiffening influence, even in large-diameter bars.

Fig. 7 shows the effect of the original casting section on the stiffness of bars 13A and 13B and 14A and 14B. Both these bars have high silicon contents and good heat-resisting properties. Here again the smaller bar in each case is better able to resist deflection than the larger bar of the same composition. While the higher-silicon bars are stiffer than the lower-silicon-content bars of the same as-cast size, the lower-silicon 0.65 in. dia. as-cast bar is stiffer than the higher-silicon 1.2 in. dia. bar.

These tests show that, for the same composition, a cast iron with coarse graphite has less resistance to deflection at high temperatures than an iron containing fine graphite. Both silicon and phosphorus increase the stiffness of coarse-graphite cast irons at the temperature of the tests.

An examination of the structures of the bars in the preceding series, however, in relation to their rigidity and composition, shows that small differences in graphite size are unimportant and have less influence on resistance to deformation at the temperature of the test than relatively small changes in composition. But an examination of the

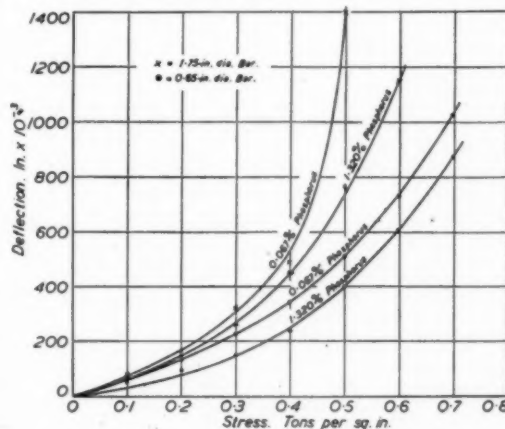


Fig. 6.—Deflection of bars of differing phosphorus contents, Series D, at 860° C. (The two lower curves also constitute Series C, high- and low-phosphorus contents).

results obtained from the bars of Series D shows that large differences in graphite size have a greater influence on rigidity than comparatively large differences in composition.

### The Rigidity of Carbon Steels at 850° C.

Three plain carbon steels, forming Series E, were tested in order to obtain a comparison between their resistance to deflection at 850° C. and that of cast iron. They had typical low, medium and high carbon contents, the analyses being given in Table IV.

TABLE IV.  
COMPOSITIONS OF STEEL BARS, SERIES E (INCREASING CARBON CONTENTS).

No.	C, %	Si, %	Mn, %	S, %	P, %
15	0.02	0.002	0.40	0.062	0.061
16	0.46	0.062	0.64	0.034	0.008
17	0.84	0.164	0.31	0.035	0.025

The test bars were machined from normalised steel rod, 0.75 in. in dia.

The deflections of these bars are shown in Fig. 8. It will be noted that the 0.02% carbon steel gave a deflection curve somewhat different from those obtained on the cast irons. Deflection is at first fairly rapid and then slows up, finally becoming rapid again. A possible explanation for this was found when a section from the parallel part of the bar after test was examined under the microscope. This showed that crystal growth had taken place to a very considerable extent. It appears probable that, as the crystals became larger, the resistance of the bar to deflection at high temperatures was increased. This conclusion is supported by the results obtained on the 0.84% carbon steel: little grain growth occurred and the deflection curve of this bar is smooth. The bar scaled rapidly and the rapid deflection at the end of the test was no doubt due to wastage of the specimen.

When these results are compared with those for the cast irons, it is found that the high-carbon (0.8%) steel deflected considerably more than any of the cast irons tested, with the exception of those with very coarse graphite structures (large-diameter bars). The medium-carbon (0.4%) steel has a resistance to deflection comparable with that of a cast iron containing 5.75% of silicon (0.65 in. dia. bar).

### The Rigidity of Austenitic Heat-Resisting Cast Irons at 850° C.

The most important of the recently developed heat-resisting cast irons are the highly alloyed austenitic irons known as Ni-Resist and Nicrosilal. The former contains nickel, copper and chromium, and the latter nickel, silicon and chromium. Both types of iron are made in a range of compositions to suit various conditions of service. Increasing the chromium content usually results in an increased resistance to scaling and growth, but high chromium renders the metal hard and practically unmachinable in the as-cast state. Two irons of each type, with high and low chromium contents, were tested, the compositions for this Series (F) being as given in Table V.

TABLE V.  
COMPOSITIONS OF ALLOY HEAT-RESISTING IRONS, SERIES F.

No.	T.C., %	Si, %	Mn, %	S, %	P, %	Ni, %	Cr, %	Cu, %
18	2.51	1.63	0.53	0.023	0.070	16.40	2.51	7.35
19	1.79	3.90	0.76	0.027	0.033	17.13	1.95	7.10
20	2.23	2.00	0.54	0.029	0.190	15.74	11.95	7.10
21	2.18	4.91	0.49	0.039	0.031	18.65	7.25	..

The resistance of these irons to deflection under load at high temperatures is shown in Fig. 9. The higher-chromium bars of each type are more rigid than those

lower in chromium. The higher-silicon material offers a greater resistance to deflection than the lower-silicon bars in both the high- and low-chromium compositions. Evidence is available that in irons of this composition carbide is deposited from the solid solution in the early stages of heating. It is possible that the resistance of the bar to deflection would be reduced while this structural change was taking place. It would appear that irons of this type should be well annealed at a temperature of 850-900° C. before being put into service. These tests show that austenitic high-silicon nickel irons are more rigid at high temperatures than austenitic copper-nickel irons, and that additions of chromium increase the stiffness of austenitic cast irons at 850° C.

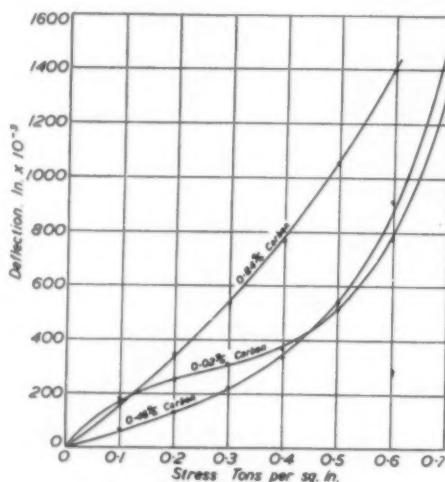


Fig. 8.—Deflection of steel bars, Series E, at 850° C.

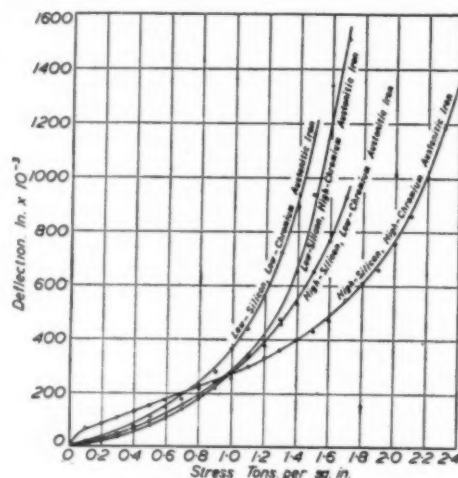


Fig. 9.—Deflection of Series F bars at 850° C.

In discussing the conclusions resulting from this investigation, the author states that in using the data obtained from these tests in deciding on the most suitable type of iron for service at high temperatures, the conditions of service must be taken into account. If, for example, the service conditions entail heating the casting slowly to a uniform temperature, it is thought that an iron which is highly resistant to deflection will give better service than one which is less resistant. On the other hand, if the service conditions are such that the casting is subjected to steep temperature gradients, then it is possible that some stiffness must be sacrificed, and a less rigid iron will be better able to withstand these conditions. It is known, for example, that the high-silicon cast irons, shown to be very resistant to deflection at high temperatures, are susceptible to cracking under conditions where temperature gradients exist, while hematite irons with a coarse graphite structure give good service under conditions where considerable and rapid changes in temperature occur.

### An Industrial Radiology Group

THE formation of an Industrial Radiology Group under the auspices of the Institute of Physics is announced. Its object is to provide a medium for the exchange of information on the practice of radiography and X-ray crystallographic analysis in industry. A committee has been appointed representing those employing X-rays in industry and the manufacturers of industrial X-ray apparatus and films. Membership of the Group will be open to all interested, whether at present members of the Institute of Physics or not. Fuller details will be published as soon as the Constitution has been formulated. Those interested may register their names with the Honorary Secretary of the Group, Dr. L. Mullins, A.Inst.P., of the Research Laboratories, Kodak Ltd., Harrow, Middlesex, who will send further information as soon as possible.

# Surface Hardening by Induction

*The success achieved in surface hardening as a result of research and development has led to increasing attention being given to this subject, and in recent years hardening has been successfully accomplished by induction heating and quenching. Developments in this new field are now of such a character that where speed, accuracy and control are important, the claims of induction heating and hardening should be considered. This method of treatment shows a marked advantage in quality and a reduction in overall cost. Results are given of an investigation on the subject, together with a discussion on the behaviour of steel heated by induction.*

**S**OME considerable time has elapsed since high-frequency currents were first used in metallurgy for the purpose of melting metals. Recently there has been a great increase in the use of such currents in the various processes of heat treatment of metals,<sup>1</sup> and the tendency to apply them is growing. Certainly where speed, accuracy and control are important, the results that can be achieved by induction heating should be given careful consideration. Increasing research and development in this field, as well as the experience gained in adopting the process in production indicates that induction hardening is justified by a marked advantage in quality, a decrease in overall cost, and by the fact that its adoption enables hardening problems to be solved that are not readily solved by any other means. Further data of this subject, together with a discussion on the behaviour of steel heated by induction, are given by Osborn<sup>2</sup> which merit special reference.

High-frequency induction heating is stated by this worker to be ideal for localised surface hardening of crankshafts and a wide variety of machine parts. It produces the desired magnitude and depth of hardness, essential metallurgical structure of core, demarcation zone and hardened case, with a practical lack of distortion and no scale formation. It permits equipment design which warrants mechanisation of the whole operation to fulfil production line requirements. Time cycles of only a few seconds are maintained by automatic regulation of power and split-second heating and quenching intervals indispensable to the creation of facsimile results of exacting specifications. Induction hardening equipment permits the operator to surface harden only the required part of almost any steel object and thus maintain the original ductility and strength; to harden articles of intricate design which are practically impossible of treatment in any other way; to eliminate usual expensive pre-treatment such as copper plating and carburising and costly subsequent straightening and cleaning operations; to cut down on material cost by having a wide selection of steels from which to choose; and to harden a fully machined component with the necessity for a subsequent finishing operation.

## Heating by Induction

By this method the heating is accomplished by the use of high-frequency currents. Specially chosen frequencies from 2,000 to 10,000 cycles and upward of 100,000 cycles are being used extensively. Current of this nature, when caused to flow through an inductor, will produce a high-frequency magnetic field within the region of the inductor. When a magnetic material, such as steel, is placed within this field there is a dissipation of energy in the steel which produces heat. The molecules within the steel attempt to align themselves with the polarity of the field, and with this changing thousands of times per second an enormous amount of molecular friction is developed as a result of the

natural tendency for the steel to resist the changes. In this manner the electric energy is transformed, through the medium of friction, into heat. Another inherent characteristic of high-frequency current, however, is to concentrate on the surface of its conductor, thus only the surface layers become heated. This phenomenon, called skin effect, is a function of the frequency, and, other things being equal, higher frequencies are effective at shallower depths. The frictional action producing the heat is called hysteresis, and is obviously dependent upon the magnetic qualities of the steel. Thus, when the temperature has passed the critical point at which the steel becomes non-magnetic, all hysteretic heat ceases. There is an additional source of heat due to eddy currents which occur as a result of the flux changes and large currents much the same as eddy swirls in a rapidly moving stream of water. With the resistance of the steel increasing with increase in temperature, the intensity of the eddy current effect is decreased as the steel becomes heated, and is only a fraction of its "cold" original value when the proper quenching temperature is reached.

When the temperature of an inductively heated steel bar arrives at the critical, all heating due to hysteresis ceases, and that due to eddy currents continues at a greatly reduced rate. Since the entire action goes on in the surface layers, only that portion is affected. The original core properties are maintained with the surface hardening accomplished by quenching when complete carbide solution has been attained in the surface areas. Continued application of power causes an increase in depth of hardening, because as each layer of steel is brought to temperatures the current density shifts to the layer beneath which offers a lower resistance.

From the foregoing it will be obvious that the selection of the proper frequency and control of power and heating time will make possible the fulfilment of any desired specification of surface hardening.

## Metallurgical Considerations

The behaviour of steel when heated by induction is unusual and the results obtained are of considerable interest. Carbide solution rates of less than a second, higher hardness than is produced by furnace treatment and a nodular type of martensite are points of consideration that classify the metallurgy of induction hardening as "different." Further, surface decarburisation and appreciable grain growth do not occur because of the short heating cycle.

Induction hardening produces a hardness which is maintained through 80 per cent. of its depth, and from there towards the core a gradual decrease through a transition zone to the original hardness of the steel as found in the core which has not been affected. The bond is thus ideal, eliminating any chance of spalling or checking. The gradual transition from the martensite of the hardened zone through the pearlitic martensitic demarcation area to the pearlite of the core is readily shown by photomicrographs of the structure of steel treated and the hardness distribution is seen in Fig. 1.

Metallurgists who have studied the matter agree that complete carbon solution can be accomplished in a relatively

1 E. F. Northrup: "Practical Application of Induction Heating to Solid Materials," *Steel*, 6th and 20th March, 1933, pp. 21 and 23; also G. Babat and M. Losinsky: "Surface Tempering of Steel by means of High-frequency Currents," *Revue Generale de l'Electricite*, 1938, vol. 44, p. 495; and G. Babat and M. Losinsky: "Surface Hardening of Tools," *Stanki i Instrument (U.S.S.R.)*, 1938 (No. 12) and 1939 (No. 6). "Heat Treatment of Steel by High-frequency Currents," by Babat and Losinsky, *Jour. Inst. Elec. Eng.*, 86, 1940, pp. 161-8.

2 H. B. Osborn, Jun. The Electrochemical Society, General Meeting, April, 1941 (Preprint 79-24).



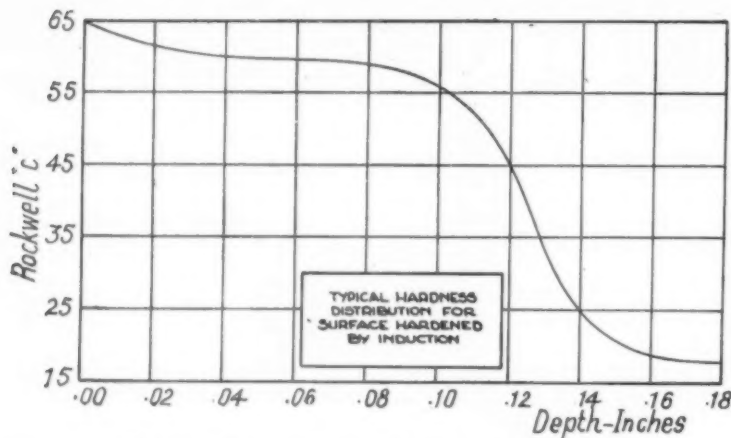


Fig. 1.—Hardness distribution for surfaces hardened by induction.

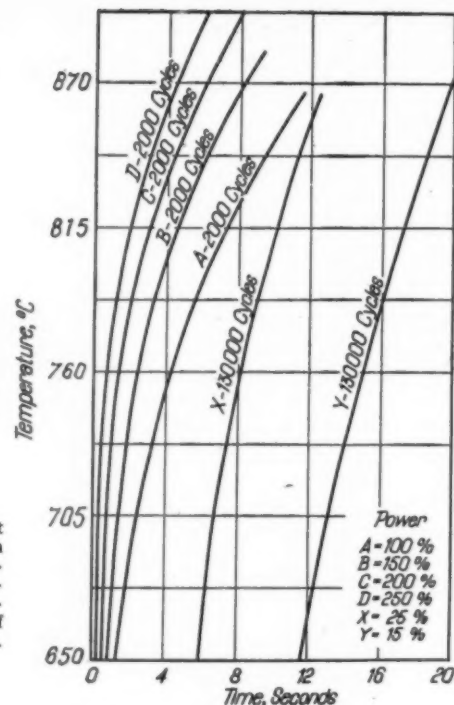
short time. Recent research data<sup>3</sup> demonstrate the solution rate to be of the order of several seconds. Induction hardening further indicates that under proper conditions less than one second is required for complete transformation to the austenitic condition as evidenced by maximum hardness and the absence of carbides in the hardened zone of such steels as the 0.5 per cent. carbon steels, etc. The prior treatment of the steel must of necessity be of such a nature as to produce desirable structure. The foregoing conclusion on carbide solution rates is based on the fact that a total heating time of two or three seconds produces temperatures in excess of the critical for only a fraction of that time. Data are available, however, where maximum hardness has been attained with a total heating time of 0.6 sec., of which 0.2 sec. was the time above the lower critical point.

In view of the extremely rapid transformation of pearlite to austenite accomplished by induction heating and the tendency for this to occur between the lower and upper critical points, a considerable amount of free ferrite might be anticipated. This, however, is not the case unless the heating is stopped at the instant diffusion has been completed within the ferrite boundaries. There is a preferential removal of carbides over ferrite, and a major portion of the ferrite persists until most of the carbides have become diffused. The next step in this rapid diffusional process involves the removal of free ferrite and the formation of a fine homogeneous structure which is retained in quenching.

In the attainment of maximum hardness Osborn states that it seems reasonable to assume that complete carbide solution and thorough homogeneity has been achieved. Not only must the temperature be sufficient to allow this diffusion to begin but the time must also lend itself to the fulfilment of completeness. Low carbon areas and grain boundaries must have been eliminated as well as any original ferrite. Heating by means of an induced high-frequency current apparently has a stimulating effect on carbide solution and the production of a homogeneous austenitic condition. Not only is the time requirement cut down but a further refinement occurs which has the ultimate result of higher hardness than is obtainable on an identical piece which has been furnace heated and quenched to the maximum hardness of furnace hardening.

The structure typical of an induction hardened area has a characteristic appearance. The usual acicular martensitic structure resulting from conventional methods is definitely absent. Instead is found a more homogeneous structure; a nodular martensite of obvious greater fineness.

Fig. 2—Effect of power on surface temperature-time relationship of 1 in. dia. bar.



#### Carbide Diffusion

A series of tests was undertaken to study the rate at which carbide solution takes place during the heating of steel by electrical induction. A fine grained steel was used having the following analysis:—

C.	Mn.	P.	S.	Cr.
0.501	0.890	0.016	0.026	0.290

Test bars 1 in. in diameter and 5 in. long were turned from quartered 2½ in. diameter stock, and the central 2 in. of the 5 in. length turned to an oversize ½ in. diameter with ⅛ in. fillet. After hardening the small diameters they were ground to 0.505 in. for tensile tests so that physical tests could be run if desired. This diameter was selected because it was large enough to give positive results and show results not always noticeable in extremely small pieces. At the frequency employed there would be no tendency to have the heat localised in the surface areas. Further, this diameter is well within the "critical size" and may be effectively centre quenched. Thus, in most cases, the entire radius was produced as a transition zone, there being a differential of hardness and structure from the surface to the centre of the bar.

The inductor used was a split block, 1½ in. wide and with a ⅛ in. hole. Each piece was hardened at 2,000 cycles and with a controlled power input to the experimental equipment. With power input "A" taken as 100 per cent., "B" represents 150 per cent., "C" 200 per cent. and "D" 250 per cent. An accurate timing mechanism was used, and quenching by jets through orifices in the inductor was performed the instant the power was turned off, the entire cycle being automatically controlled. Quenching continued long enough to bring the test bar to approximately 38° C. Drawing at 99° C. for one hour followed in order to relieve strains.

Each sample was cut through the centre of the hardened areas after hardness readings had been taken on the circumference at that location. The additional Rockwell readings were made on the polished cut face on circles circumscribed at 1.5, 3.0 and 5.0 mm. from the outer edge and on the centre edge. Table I gives all pertinent data.

Due to the extremely short heating cycles it was not practical to make maximum temperature measurements on each test piece, and yet a reasonably accurate knowledge of this temperature was desirable. Hence, a temperature-

<sup>3</sup> R. H. Lauderdale and O. B. Harder, "Study of Carbide Solution in Hypo-eutectoid Plain Carbon and Low Alloy Commercial Steels," *Trans. Am. Soc. Metals*, **27**, 605 (1939).

time relationship was established so that, for a given power input, the temperature at any instant could be determined. An optical pyrometer was set for definite temperature, starting at 760° C. and increasing in increments of 14° C. up to 870° C., and sighted on the surface of a list specimen through a slot in the inductor block. In every case a test bar was heated from room temperature, and the time measured (to within 0.10 sec.) for it to reach the pre-selected temperature for each power setting. More than one determination was made at each setting so that an average could be taken representative of each temperature-time relationship. The results of these runs are plotted in Fig. 2, with curves extrapolated from 760° to 650° C.

Realising the accuracy of an optical pyrometer to be dependent upon operating conditions, extreme care was exercised in using it. When readings were taken for the data given, the line of sight from the pyrometer to the heated specimen was shielded with a tube in order to eliminate all extraneous light. The scale setting on the pyrometer was adjusted and checked under conditions as identical with the test procedure as possible. A small piece of steel, with essentially the same surface characteristics as the specimen bars, was drilled to accommodate a platinum thermo-couple. The hole was filled with "phosphor" which at the temperature measured formed a liquid metal bath for the thermo-couple inserted in the well. The steel was then heated in an inductor, and when a constant temperature had been reached readings were taken with the optical pyrometer sighted at the area adjacent to the well and on a semi-precision potentiometer which was connected to the thermo-couple. No appreciable difference in readings was noticeable over the range 760° to 870° C.

TABLE I  
HARDNESS TESTS ON TREATED  $\frac{1}{2}$  IN. DIA. BAR.

Specimen No.	Power Input	Time Sec.	Rockwell "C"				
			Mm. from Edge*				Centre
			0-0	1-5	3-0	5-0	
1	A.	11.8	65.8	64.2	64.1	64.1	64.1
2	A.	9.5	65.4	63.8	63.8	63.8	63.9
3	A.	8.3	65.5	63.8	63.9	63.9	63.9
4	A.	4.6	65.5	64.8	64.3	64.0	63.7
5	A.	4.2	65.4	64.8	64.3	63.6	63.1
6	A.	3.7	64.3	64.2	62.8	54.6	48.0
9	B.	8.2	66.2	64.6	64.5	64.6	64.6
10	B.	6.8	65.9	64.2	64.2	64.1	64.0
11	B.	4.4	65.8	65.0	64.6	64.3	64.2
12	B.	3.3	65.9	65.0	64.0	63.2	62.8
13	B.	2.1	66.0	63.1	57.3	34.1	29.1
16	C.	6.0	66.0	64.2	64.1	64.2	64.3
17	C.	4.7	65.6	64.2	64.3	64.2	64.2
18	C.	3.3	65.9	65.0	64.7	64.3	64.0
19	C.	1.9	65.8	64.1	62.6	38.4	33.1
20	C.	1.3	65.4	54.7	38.9	30.1	26.3
23	C.	1.1	32.2	29.9	26.7	24.0	21.0
24	D.	2.9	65.3	64.5	64.6	64.5	64.5
25	D.	2.0	65.3	64.5	64.5	64.5	64.4
26	D.	3.0	65.7	64.7	64.6	64.6	64.6
27	D.	1.8	65.2	64.7	63.8	62.1	60.5
30	D.	0.6	65.3	51.5	37.0	26.3	16.7

\* Average of readings taken on circles spaced at distances indicated.  
0-0 mm.—30 readings .... A.—100% .... 3-0 mm.—18 readings .... C.—200%  
1-5 mm.—25 readings .... B.—150% .... 5-0 mm.—8 readings .... D.—250%  
Centre—5 readings

Specimens of Table I were examined after hardening for structure and hardening. Each sample was carefully polished and etched. Micro-examination was then made on the prepared faces at the surface, 1.5, 3.0 and 5.0 mm. from the edge, and at the centre, on eight equally spaced radii. Gradual disappearance of the carbide was apparent and complete solution is indicated for all areas showing Rockwell "C" of 65 or better. Carbide diffusion takes place within the grain boundaries before any appreciable elimination of the ferrite boundaries took place. Some specimens gave evidence of complete transformation to martensite with the original pearlite boundaries remaining undisturbed.

Calculations of the length of time the surface of many of the test bars were actually above the lower critical point yield extremely small values. Such values are in many instances less than 1.0 sec. with specimens Nos. 6, 13, 20 and 30 being of the order of 0.2 to 0.3 sec. Complete carbide solution and homogeneity was accomplished in

each, as was indicated by satisfactory hardness and lack of free ferrite and carbide in the micro-structure. The steel used in the tests described was slightly sorbitic, but the author considers that comparison with the solution rate possible in a completely pearlitic structure will demonstrate that carbide solution in a few tenths of a second is really not phenomenal.

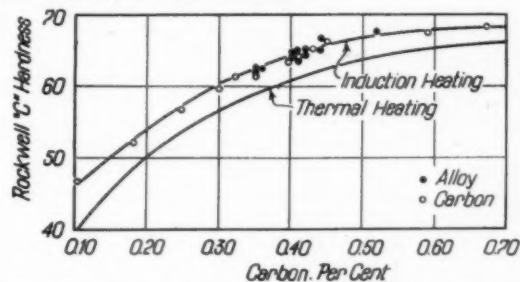


Fig. 3.—Maximum hardness obtainable for steels of varying carbon content.

The results obtained on these tests specimens are claimed to be well within any theoretical consideration of carbide solution rates, and as further confirmation, induction hardening equipment is in everyday operation, on a production basis, with complete carbide solution resulting from a heating and quenching cycle, the total time of which is less than 2 secs.

### Super-Hardness

In order to demonstrate the increased hardness obtained with induction heating a number of steels with carbon content ranging from 0.10 to 0.70% were tested. Samples were received from three different sources in sizes from 0.5 to 1.5 in. All were fine grained, and either normalised or quenched and drawn. Twelve carbon steels and twelve alloy steels made up the samples tested. Each sample was placed in a commercial inductor block and assembly and heated to approximately 10° C. above the  $A_{c3}$  and instantly quenched. The water pressure was 85 lb./sq. in. at the inlet valve, but the pressure on the surface of the test specimens was only a fraction of this amount, due to a faulty coupling; however, a drastic quench was possible. No attempt was made to ascertain whether or not the critical cooling rates had been exceeded, but the hardness results indicate that this must have been the case. Further, these results preclude the presence of an appreciable amount of retained austenite. Surface readings were taken with a Rockwell hardness tester and averaged from 13 to 15 readings for each sample. The average hardness values have been plotted in Fig. 3, giving the curve which is indicated "induction heating." The data indicated by the curve designated "thermal heating" are from purely experimental research methods and equipment, and are not representative of actual production practice results, but they serve to show that higher maximum hardnesses result when steel is heated inductively and quenched than when heated normally.

### Steel Requirements

It is not yet possible to make a definite statement regarding the types of steel for which the induction hardening method is best suited. There are certain requirements, however, which are quite obvious. The carbon content must be sufficient to produce the desired hardness, although higher hardness is possible with this method of hardening. A fine grain size is preferable yet not always essential. Due to the excessive demands made on crankshafts, it has been found advisable for such and similar components to use a heat-treated structure which is predominantly sorbitic or a normalised structure and have a grain size comparable to that of the heat-treated condition. Low carbon steels with carburised case, medium and high carbon steels—both straight carbon and alloy steels—and

also ordinary cast-iron in a malleable pearlitic condition, can all be hardened as desired. Generally speaking, any material which will respond to a heating and cooling operation may be hardened or heat-treated by induction heating.

### Equipment

Surface hardening equipment consists of an inductor, quenching auxiliaries, suitable transformers and capacitors, automatic timing controls, and a high-frequency generator. In addition, provision must be made for handling the parts treated, whether intermittently or continuously, depending upon production requirements.

The inductor may be a single turn of copper to fit the piece to be hardened, or several turns of copper tubing shaped for the same purpose. Careful design is essential to ensure maximum efficiency. Symmetrical inductors, however, may be used to surface harden unsymmetrical parts because of the natural tendency of the high frequency current to follow the contour of the piece. The quenching medium is supplied through the inductor by means of orifices which are an integral part of it. The same timing device which controls the heating cycle operates an electric quench valve and controls the quenching cycle to the same degree of accuracy.

Automatic control and accuracy are essential features in induction hardening; such precision involving exact locations of hardened areas and automatic control to within 0.1 sec. is merely a matter of equipment design. This control makes each hardening operation and hardened component uniform, and since it eliminates human error, the usual variations and mistakes, characteristic of manual control, are avoided.

Large converters of the generator type are in use for 2,000, 3,000 and 10,000 cycles at capacities up to 1,000 kw. Smaller 7.5 to 30 kw. units of the spark gap oscillator type are used at frequencies up to 100,000 cycles. The high frequency current is usually generated at high voltage, ranging from 200 to 1,000v., depending upon the particular unit. It is then transformed and fed into the inductor. The transformer is designed for the specific frequency and the inductors to be used with it. In some instances, where a multi-turn coil is employed, the transformer is eliminated and connection made directly across the generating source.

In order to obtain high efficiency, the high-frequency power factor is adjusted and maintained as near unity as possible. This is accomplished by connecting in the circuit the proper amount of capacitance. Variations in capacitor requirements are readily accommodated by a switch mechanism which provides immediate change of the number of condenser units.

The power used for each hardening operation is controlled and maintained by the field excitation of the generator. Occasionally it is found that a fixed excitation will not produce a constant power output due to the electrical characteristics of the steel changing during the rising temperature. A longer, undesirable heating cycle would result. The power is maintained constant, however, by an automatic control system which changes the external resistance of the field circuit at pre-set, split-second type intervals while the power is on.

### Indium Plating

An indium sulphate plating bath, for the application of smooth matte surface deposits, in thickness of the order of 0.0001 in. is described by Linford.\* Operation of this bath over a considerable length of time has shown it to be very stable and constant in performance within the pH range, 2.0 to 2.7. This has been accomplished by the use of a combination of soluble and insoluble anodes for maintaining a constant pH. Conditions are given for obtaining satisfactory plates on many basic metals.

### High-grade Coke from Low-grade Coal

SOVIET scientists are working out a new method for the industrial production of high-grade coke for smelting purposes from low-grade coal. A commission, headed by Professor M. A. Pavlov, has carried out experiments during the last two years at the Magnitogorsk Iron and Steel Works in the Urals, with low-grade coal obtained from the deposits in the eastern and southern parts of the Soviet Union. This work was undertaken with the object of extending the raw material base of the Soviet coke and chemical industry, and improving the quality of coke for blast furnaces.

Using data obtained by this commission, scientists of the Fuel Institute of the Academy of Sciences of the U.S.S.R. have designed an apparatus for determining the behaviour of coke in the blast furnace. By means of this device the scientists have worked out a new system for rating coke. The apparatus also makes it possible to control the process of smelting, to increase the productivity of blastfurnaces and to improve the quality of coke.

Coke obtained from low-grade coal from the Karaganda deposits in Kazakhstan and the Kzyl deposits in the Urals, as well as from a number of deposits in the Kuznetsk coal basin in Western Siberia and Donets coal basin in the Ukraine, has been tested successfully in blast furnaces. The results show, for example, that it is possible for the Magnitogorsk Iron and Steel Works, which now obtains its coal from the Kuznetsk basin, to use coal from the Karaganda basin, which is 620 miles nearer.

### The Effect of Gas Pressure on the Passivity of Iron

THE data and theories of passivity have been well reviewed by MacInnes,<sup>1</sup> who concludes that the oxide film theory has the greatest amount of supporting evidence. Wulff<sup>2</sup> and co-workers have proposed an electrochemical theory to explain passivity. To date, the electron diffraction<sup>3</sup> data have not conclusively proved or disproved the oxide film theory. Cone and Tartar<sup>4</sup> presented data showing that iron had oxygen absorbed on its surface, which could be removed by reducing the pressure to produce active iron if sulphate or nitrate ions were present in the chromic acid solutions. In a recent investigation by Crog and Hunt,<sup>5</sup> an attempt was made to determine the effect of decreased pressure on the passivity of iron in chromic acid solutions, prompted by the results obtained by Cone and Tartar.

Under the conditions of the experiments there was no observed effect. The passivity or activity of the iron was measured by the potential of the iron/chromic acid solution half-cell with a  $\text{Hg}/\text{Hg}_2\text{CrO}_4/1.0 \text{ M H}_2\text{CrO}_4$  electrode as the reference half-cell. Iron was found to be active in chromic acid solutions containing moderate concentrations of halide ions. Iron wires, when heated at red heat in a vacuum (0.01 mm. of Hg) were found to be passive in chromic acid solutions. This agrees with the reports that heating iron in nitrogen or in a vacuum causes it to become passive. Hence it would seem improbable that an absorbed film of oxygen could be the cause of the passivity. Some oxide may form when the wire is heated in a vacuum, depending on the degree of the vacuum; however, no such oxide film should form upon heating in an atmosphere of nitrogen. Therefore, if there were no oxide film on the metal surface before heating it in nitrogen, none should form during the process, and the passivity could not be due to an oxide film formed during the heating process. However, this does not preclude the possibility of the formation of such an oxide film after immersion into the chromate solution.

<sup>1</sup> MacInnes, "Principles of Electrochemistry," Reinhold Publishing Co., New York City, 1929.

<sup>2</sup> Uhlig and Wulff, Trans. Am. Inst. Mining Met. Engrs., 135, 506, 1939.

<sup>3</sup> Thomson, Proc. Roy. Soc., 128-A, 649, 1930.

<sup>4</sup> Cone and Tartar, J. Am. Chem. Soc., 59, 937, 1937.

<sup>5</sup> Crog and Hunt, General Meeting, Electrochemical Soc., 1941 (advance copy).

\* The Electrochemical Society, General Meeting, 1941 (advance copy).



## Reviews of Current Literature

### An Outline of Metallurgical Practice

SINCE the publication of the first edition of this book, about ten years ago, much progress has been made in metallurgical practice, despite the fact that the period included a severe industrial depression which undoubtedly had a retarding effect on research and the development of new processes in the metallurgical industries. But even during the worst of the depression the search for economies proceeded with considerable vigour. During the early years subsequent to the publication of the earlier edition, the metallurgical industries were faced with many complex problems, the solution of which proved to be slow and tended to delay development, but it was recognised that progress was necessary because of the vital importance of these basic industries to industrial and economic life. The progress achieved in more recent years is due, in a large measure, to the foresight displayed in times of adversity, and its effect on modern practice is admirably presented in this new edition, though the general characteristics of the first edition have been kept.

This book is produced with a view to satisfying two demands: First, to meet the desire of many engineers for a quick reference book which will give modern practice in extracting and refining most of the metals, and will give general information regarding the sources, uses and important alloys of the metals. The second demand is the assistance it provides to students who are starting their metallurgical studies with no practical experience and little or no knowledge of the subject or its literature. Such a student is bewildered when faced with the variety of processes, some obsolete, some active, and some proposed and not yet applied commercially. There is no doubt that the initial difficulties of the student and, to a lesser extent, the engineer, in grasping the fundamental principles and practices of this complex subject are very considerable, and any work of this character which facilitates study and gives a clear conception of modern practices in metallurgy serves a very useful purpose, as it reduces the possibility of confusion that is almost inseparable from a complete treatise at the preliminary stage.

Most metals do not occur in the earth's crust in the native or metallic state, but as mineral sulphides or oxides, and in order to separate them from the elements with which they are combined, various processes are involved which are conveniently classified in stages. Thus, beginning with the mined mineral, some need to be concentrated to effect separation into groups; roasting may be necessary, as in the case of sulphide ores; subsequently the rich ore or concentrates are smelted and the product is refined to remove impurities. These various stages are clearly discussed, and the numerous exceptions to this general procedure are considered when the individual metals are discussed.

Copper, the first metal discussed, is treated at much greater length than the other non-ferrous metals. This is doubtless due to the fact that certain general operations, such as roasting, are described and illustrated here and merely referred to in discussing operations with other metals. In addition to copper, the discussion on which occupies 131 pages, lead, zinc, aluminium, nickel, tin, mercury, antimony, arsenic, bismuth, cadmium, cobalt, magnesium, beryllium, gold, silver, platinum, chromium, tungsten, manganese, vanadium, molybdenum, zirconium, iron and steel, and non-ferrous alloys are discussed in the order given.

The chapter allocated to iron and steel provides a comprehensive section, occupying 127 pages, and each chapter is sub-divided under convenient headings. Thus, on the subject of iron and steel, the occurrence and sources of iron ores are discussed, followed by beneficiation of iron ores; smelting in the blast furnace, with discussions on

the modern blast furnace, blast stoves, ore charge and its preparation, fuel and flux, blowing-in the furnace, charging, furnace reactions, products of the blast furnace; production of steel in which the various processes are discussed; production of wrought iron; iron foundry practice; malleable cast iron; composition of common steels; the working of steel.

The section at the end of the book devoted to non-ferrous alloys has been enlarged to include alloys including zirconium and beryllium, and the equilibrium diagrams have been brought up to date. The same method of treatment used in the first edition has been retained. An interesting feature is the suggestions for supplementary reading appended to each section to guide students in pursuing researches with any metal. The book is well illustrated, containing over 400 line drawings and photographic reproductions, many of which are used primarily to assist those lacking plant experience and also to limit the need for descriptions of processes and apparatus. The book is admirably produced and can be confidently recommended to meet the demands the author had in mind.

By Carle R. Hayward, Professor of Metallurgy, Massachusetts Institute of Technology. Published by Chapman & Hall Ltd., 11, Henrietta Street, London, W.C.2., price 38s. net.

### Metal Aircraft Production

THE first edition of this book was published in 1932, a revised and enlarged edition was published in 1934, and a third revised and enlarged edition appeared in 1937, the demand for which necessitated a reprint in the same, and the present, the fourth edition, is further revised and enlarged. Out-of-date material has been eliminated except where it is of basic technical interest, and much new matter, particularly relating to American aircraft, has been added. Particulars of aircraft of the belligerent countries are of necessity scrappy. This is especially true of German aircraft, as the revision had been completed before many specimens fell into British hands. Despite difficulties, however, which the author must have encountered, this is a comprehensive treatise on the design and construction of the major components of a large number of representative aircraft, and it forms an authoritative work in which are discussed the development of metal aircraft; materials; main planes and main plane structures; fuselages; flying boat hulls and seaplane floats; subsidiary structures; workshop processes and detail design; corrosion; and riveting.

The basic structure of British, American, German, French, Polish and Czechoslovakian planes are described with remarkable clarity. The wide variety of composite sections, extruded structural shapes and rolled structural shapes, now regularly used in aircraft construction make selection difficult, but in this book the author has managed to amplify the text with a large number of line illustrations which greatly assist the assimilation of the matter. Comparisons in span constructions are emphasised, and as much care is taken in the design and construction of subsidiary structures and details as with the main plane structures and fuselages. The author has given considerable attention to detail, so ably is the matter presented, however, that the book is not only informative, it is interesting. It gives a very comprehensive review of developments in this field, and gives aeronautical engineers and students very full information on modern international practice in metal aircraft construction. The last chapter is a useful addition, presenting tables of specifications and strengths of materials.

By Marcus Langley, F.R.Ae.S., M.Inst.Ae.S., A.M.Inst. N.A. Published by Sir Isaac Pitman & Sons Ltd., Parker Street, Kingsway, London, W.C.2., price 15s. net.

## Avoiding Galvanic Corrosion in Light Alloy Products

(Continued from page 46)

adhesive is thoroughly dry the canvas is coated with marine glue or a compound such as Duralac, as are also the contacting surfaces of the steel plate. The whole is then bolted together with the provision of fibre washers under the bolt head and nut. It should be noted that the canvas is allowed to project past the end of the steel to minimise the possibility of moisture bridging the gap.

It will be appreciated that such a procedure would only be adopted if the possibility of galvanic action were severe, and that a more normal procedure designed simply as a safeguard would be to coat all faying surfaces and the inside of the bolt holes with marine glue or Duralac before assembly, with omission of the canvas insert.

The foregoing are simple illustrations capable of solving many industrial applications by adoption of the method, but some possible cases will require the exercise of considerable ingenuity on the part of the designer. As an instance, consider the hypothetical case of an apparatus of which the body is required to be in a salt water, corrosion-resisting aluminium alloy to save weight, while there is a head attached which must receive a flow of salt water from the light metal body, but which must at the same time be in another metal, since it is a secondary function of the head to pass another flow of liquid which the aluminium alloy will not resist. A possible method of solving this problem is diagrammatically illustrated in Fig. 4.

The secret of successful service in an application of this type is complete insulation, so that at no point in the construction is there a metal to metal contact between the light alloy and the dissimilar metal. The enlarged view of the flange connection shown in Fig. 5 will demonstrate clearly the method recommended.

As will be seen, the two flanges are separated by a non-metallic insert, and the bolts are prevented from making metallic contact with either of the flanges by the provision of an insulating sleeve and two insulating washers.

This completely breaks the circuit in the immediate danger area, but precautions should also be taken to ascertain that there is no completion of circuit between the head and the body at any other point. If, for the sake of illustration, there is a metal tube conveying liquid from the head to some point in the body, this should be broken at some place along its length, shortened, say, by an inch and the connection made good with rubber hose.

As a last example, consideration will now be given to the use of a third "sacrificed" metal in an application which has proved very successful in service.

This is in the case of small sea-going craft having the hulls built entirely from aluminium alloy but with propeller shafts of, for instance, Monel metal and screws of bronze. With sea water as the conducting liquid, this is an instance where galvanic action would quickly cause damage to the light alloy sheets at the stern of the vessel, but it is also a case in which knowledge of the mechanism of galvanic action has enabled precautions to be taken that have completely eliminated any risk.

The method adopted is shown diagrammatically in Fig. 6. Insulation of the shaft and screw from the hull is made as complete as possible by the use of cutless rubber bearings in the stern tube and shaft housing, while plates of pure zinc are fixed in metallic contact with the light alloy at these points. In practice, it is found that the zinc plates are gradually consumed or "sacrificed," but that the aluminium alloy is protected from galvanic action. This protection with the aid of the zinc plates can be prolonged indefinitely if the zinc is renewed every few months as the need arises.

In passing, it should be noted that the life of the zinc plates will depend largely on the method by which they

are attached to the light alloy. If, for instance, they are attached by means of steel studs as is usually done, it is likely that the majority of the action on the zinc will be concentrated around the steel nuts, so that eventually the plate will drop off while still having many months of useful life left. An improved method which the writer has tried is to regard the zinc plates and their holding studs as a separate instance of dissimilar metals and to carry out the attachment as in Fig. 7. By this method the zinc is enabled to wear away more regularly and the maximum useful life can be obtained.

The examples given will serve to show some of the means that can be adopted to combat galvanic action, and by variations of the methods described it is possible, in almost every case, greatly to minimise or prevent such action in composite products.

Finally, there are a number of other points not previously mentioned that are important when considering the design of composite components. These are as follows:

- (a) Galvanic action does not, in the majority of cases, travel far from its source, i.e., if a bolt of stainless steel or other dissimilar metal is screwed into an aluminium alloy plate, and the whole is immersed in sea water, the action will be concentrated immediately in the vicinity of the bolt, and will not be spread over the entire plate. Local insulation can thus minimise concentration of attack.
- (b) If the area of aluminium alloy is smaller than that of the dissimilar metal, galvanic action on the light metal will be more pronounced than in the reverse case. Special attention to insulation is necessary.
- (c) In a welded construction a welding rod of the same composition as the metal being welded should be used wherever possible. If, as is often the case, an aluminium-copper alloy is welded with an aluminium-silicon alloy welding rod, galvanic attack at the weld may be experienced.
- (d) Do not use so-called aluminium solders in any applications where galvanic conditions may ensue. Such solders contain little or no aluminium, and are in fact, dissimilar metals.

By consideration of the metals series given, and to the principles of insulation in design, it should be possible, in the manufacture of the majority of composite light alloy components, to ensure that mysterious service failures, due in a high percentage of cases to galvanic action, will be greatly minimised or entirely avoided.

## Prestcold Oil Coolers

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